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Patentanmeldung Nr. Patent application No. Demande de brevet n°

03015731.7

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R C van Dijk



Anmeldung Nr:
Application no.: 03015731.7
Demande no:

Anmeldetag:
Date of filing: 10.07.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
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substituted Anthracenes

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C07C43/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

**Merck Patent Gesellschaft
mit beschränkter Haftung
64271 Darmstadt**

**EPO - Munich
24
10. Juli 2003**

Substituted Anthracenes

Substituted Anthracenes

Field of the Invention

5 The invention relates to novel substituted anthracenes, to their use in liquid crystal, light-emitting or semiconducting materials and devices, in anisotropic polymers, optical, electrooptical, decorative, security, cosmetic, diagnostic, electric, electronic, charge transport, semiconductor, optical recording, electroluminescent,
10 photoconductor or electrophotographic applications, and to liquid crystal, light-emitting and semiconducting materials, polymers and devices comprising them.

Background and Prior Art

15 In the search for novel materials for organic light-emitting diode (OLED), organic field emission transistor (OFET) and emissive liquid crystal display (eLCD) applications, a number of basic structure considerations are necessary:

- 20 • Materials should possess a highly conjugated structure, with a long UV wavelength absorbing chromophore. This facilitates efficient excitation of the molecule, either by photons or electrons, giving rise to photo- or electroluminescence.
- 25 • In order to be compatible with calamitic liquid crystalline media, and in order to be efficient emitters of polarised light, either by photo or electroluminescence, materials should ideally be rod-shaped molecules.
- 30 • The rod-like molecules should comprise lateral substituents in order to modify the melting point, the nature of mesophases and the solubility in common solvents or liquid crystal hosts.

35 It is generally known in LC structure property relationships that lateral substituents, such as halo, alkyl, alkoxy groups, in calamitic LC's reduce the melting point, modify the mesophase and improve the solubility. See for example Gray, G.W., Hird, M. & Toyne, K.J., 1991,

Mol. Cryst. Liq. Cryst., 204, 43. Additionally it is known that for OLED polymers the lateral chains improve solubility as well as acting as a modifier to the electroluminescence properties. See for example Kraft, A., Grimsdale, A.C. & Holmes, A.B., 1998 Angewandte Chemie Intl. Edn. Engl., 37, 402 - 428.

There are many examples of liquid crystals with extended conjugated structures in prior art. Many of these find use as additives for high birefringence mixtures, useful especially in the infrared range of the electromagnetic spectrum, like for example the diphenyldiacetylene LC compounds disclosed in US 6,312,618.

There are additionally prior art references to the use of fused ring structures as molecular components of liquid crystals, especially naphthalenes. In the emerging field of organic charge transport materials, the work of Hanna is especially relevant, as it details the advantage of smectic LC ordering on charge transport in phenyl naphthalene structures. See for example Y. Toko, M. Funahashi, J. Hanna, Japan. Proceedings of SPIE-The International Society for Optical Engineering (2003), 4800 (Organic Light-Emitting Materials and Devices VI), 229-237; N. Yoshimoto, J. Hanna, Adv. Mater. 2002, 14(13-14), 988-991; H. Maeda, M. Funahashi, J. Hanna, Materials Research Society Symposium Proceedings (2000), 598 (Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials V), BB3.61/1-BB3.61/6.

Additionally US 2001-0048982 teaches emissive LCD devices that include phenyl naphthalene materials.

Time of flight measurements show improvements to charge carrier mobility as smectic order increases. The reason for improved charge mobility is thought to be that smectic ordering allows closer packing of the planar aromatic cores.

However, many prior art materials are unsuitable as components of OLED or other optoelectronic devices, because the extent of their

conjugation is limited, resulting in poor excitation properties for efficient electroluminescence.

5 The use of polymerisable LCs, also known as reactive mesogens (RM), for OLED and OFET applications, in particular as a means of producing polarised emission, has also been reported in prior art. For example, US-A-2003/0018097 discloses the use of a reactive RM comprising a 9,9'-dialkylfluorene group that is substituted in 2- and 7-
10 position with a 5-phenyl-thiophene-2-yl group. Bacher, Bradley et al., J. Mat. Chem. 1999, 9, p.2985 disclose a distyrylbenzene RM and its use for a polarised electroluminescence (EL) device. O'Neill et al., J. Appl. Phys. 2003, 93(3), p.1465 disclose the use of and references contained within, disclose the use of some reactive mesogen species for polarised light emission.

15 However, the RMs cited in these references comprise an acrylate or 1-vinyl-allyloxycarbonyl group as polymerisable group, which can be disadvantageous for efficient OLED emission, as the carbonyl group is known to quench electroluminescence (see List et al., Adv. Mater. 2002, 14(5), p.374). Additionally, these references report that
20 residues of the photoinitiator used for polymerisation of the RMs can have a detrimental effect on electroluminescence. Meerholz et al., Nature 2003, 421, p. 829, however, report that it is possible to use a cationic photoinitiator process to produce a cross linked polymer
25 OLED based on oxetane photopolymerisable groups without detriment to the OLED electroluminescent properties.

30 One aim of the present invention is to provide novel mesogenic or liquid crystalline compounds with a rod-shaped molecular structure which are optionally polymerisable, which do not have the drawbacks of prior art or do exhibit them to a lesser extent, have improved properties, and are especially suitable for liquid crystal, semiconducting and light-emitting applications, like LCD, eLCD, OLED and OFET devices.

35

5 The novel compounds should fulfill the above-mentioned basic structure requirements for OLED, OFET and eLCD use. Preferably they should exhibit a liquid crystal phase over a broad temperature range, allow close packing in a highly ordered mesophase, and show good charge transport and light emission properties.

Another aim of the invention is to extend the pool of materials suitable for LCD, OLED and OFET uses that are available to the expert.

10 Another aim of the invention is to provide advantageous uses for the novel compounds, such as liquid crystal, light emitting and semiconducting materials and devices, in particular LCDs, eLCDs, OLEDs and OFETs, anisotropic polymers; optical, electrooptical, decorative, security, cosmetic, diagnostic, electric, electronic, charge
15 transport, semiconductor, optical recording, electroluminescent, photoconductor and electrophotographic applications.

20 Another aim of the invention is to provide improved LC, OLED and OFET materials; polymers and devices with that do not have the drawbacks of LC media known from prior art.

25 Another aim of the invention is to provide new oligo- and polymers for use as semiconductors or charge transport materials, which are easy to synthesize, have high charge mobility, good processibility and improved oxidative stability.

Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

30 The inventors of the present invention have found that the above mentioned drawbacks can be overcome by providing novel mesogenic anthracene derivatives as claimed in claim 1. These compounds have advantageous properties and are especially suitable for use in LCD, eLCD, OLED and OFET devices.

35

The compounds according to the present invention, which include anthracene as a major component of the aromatic core, pack in a very efficient manner and produce very efficient charge transport, thus making them good candidate materials for OFET use.

5 Additionally, the anthracene moiety is highly fluorescent on irradiation with UV light, both as a solution and as a thin solid film.

Furthermore, the inventors have found that monomers, oligomers and polymers based on anthracene modified with photostabilising substituents in 9- and 10-position are suitable as semiconductors or charge transport materials. The presence of an alkoxy group R in the 9- and 10-positions of the anthracene ring system increase the solubility and thus the processability of the polyanthracenes.

15 EP 1 090 911 A2 discloses a bis(aminostyryl) anthracene compound emitting yellow or red light. US 6,495,274 discloses an OLED device comprising a bis(aminostyryl) anthracene compound. However, these materials are not likely to be mesogenic as they do not have terminal chains, additionally they cannot be cross linked, as they
20 have no reactive component. This would lead to serious deficiencies in device processing.

Summary of the Invention

25 The invention relates to compounds, including reactive and non-reactive monomers, oligomers and polymers, comprising one or more identical or different groups of formula I



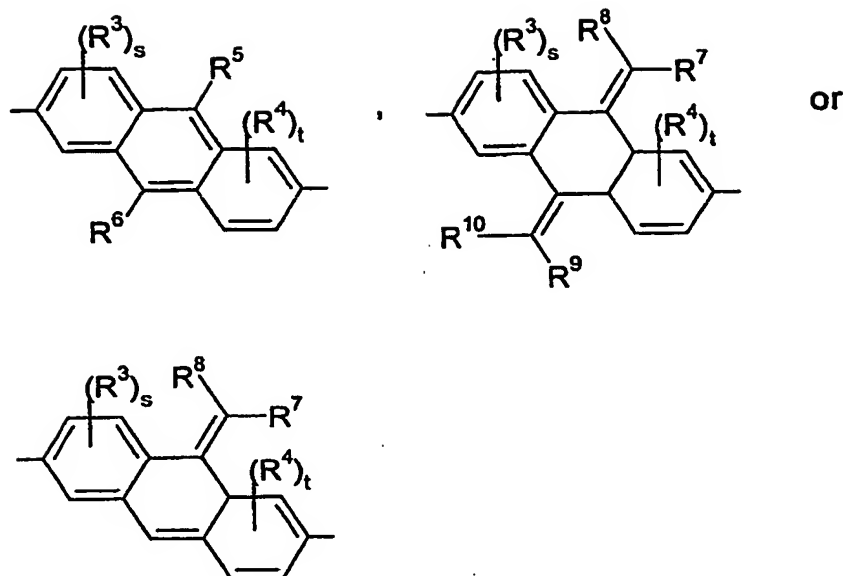
I

30

wherein

G is, in case of multiple occurrence independently of one another,

35



20

25

R^3 to R^{10} are independently of each other F, Cl, Br, I, CN, NO_2 , NCS, SF_5 or straight chain or branched alkyl having 1 to 30 C-atoms that is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, and in which one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, - NR^0 -, - $\text{SiR}^0\text{R}^{00}$ -, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, - $\text{CY}^1=\text{CY}^2$ - or - $\text{C}\equiv\text{C}$ - in such a manner that O and/or S atoms are not linked directly to one another, or P-Sp,

R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

30 P is a polymerisable or reactive group,

Sp is a spacer group or a single bond,

s and t are independently of each other 0, 1, 2 or 3,

35

g is, in case of multiple occurrence independently of one another, 1, 2 or 3.

5 The invention further relates to an LC medium comprising at least one compound according to the present invention.

The invention further relates to a polymerisable LC material comprising at least one compound according to the present invention.

10 The invention further relates to a polymerisable LC material comprising at least one compound according to the present invention and optionally at least one further compound, wherein at least one of said compounds is polymerisable.

15 The invention further relates to a polymer obtained by polymerising a compound or a polymerisable LC material as described above and below.

20 The invention further relates to an anisotropic polymer obtained by polymerising a compound or a polymerisable LC material as described above and below in its oriented state, preferably in form of a film.

25 The invention further relates to a semiconductor or charge transport material comprising at least one compound or a polymerisable LC material or polymer as described above and below.

30 The invention further relates to a light-emissive material comprising at least one compound or a polymerisable LC material or polymer as described above and below.

35 The invention further relates to the use of compounds; mono-, oligo- and polymers, LC materials, semiconductor or light-emitting materials, polymerisable materials, polymers or polymer films as described above and below in electrooptical displays, LCDs, eLCDs,

optical films, polarisers, compensators, beam splitters, reflective films, alignment layers, colour filters, holographic elements, hot stamping foils, coloured images, decorative or security markings e.g. for consumer objects or documents of value, LC pigments, adhesives, synthetic resins with anisotropic mechanical properties, cosmetics, pharmaceuticals, diagnostics, nonlinear optics, optical information storage, as chiral dopants, in electronic devices like for example OFETs as components of integrated circuits (IC), as thin film transistors (TFT) in flat panel display applications or for Radio Frequency Identification (RFID) tags, in semiconducting or light-emitting components of organic light emitting diode (OLED) applications, electroluminescent displays or backlights of LCDs, for photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors, or for electrophotographic applications or electrophotographic recording or as alignment layer in LCD or OLED devices.

The invention further relates to a semiconducting component, for example in OLED applications like electroluminescent displays or backlights of, e.g., liquid crystal displays, in photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors and for electrophotographic applications, comprising one or more compounds, mono-, oligo- or polymers according to the invention.

The invention further relates to an optical, electrooptical or electronic device, in particular an LCD, eLCD, OLED, OFET, IC, TFT or alignment layer that comprises a compound, mono-, oligo- or polymer, an LC material, semiconductor or light-emitting material, a polymerisable material, polymer or polymer film as described above and below.

The invention further relates to a TFT or TFT array for flat panel displays, RFID tag, electroluminescent display or backlight comprising a compound, material, polymer or device, in particular comprising an LCD, eLCD, OFET, OLED, IC or TFT as described above and below.

The invention further relates to a security marking or device comprising a compound, material, polymer or device, in particular an LCD, OLED, OFET or RFID tag as described above and below.

5

Definition of Terms

The terms 'liquid crystalline or mesogenic material' or 'liquid crystalline or mesogenic compound' means materials or compounds comprising one or more rod-shaped, lath-shaped or disk-shaped mesogenic groups, i.e., groups with the ability to induce LC phase behaviour. The compounds or materials comprising mesogenic groups do not necessarily have to exhibit an LC phase themselves. It is also possible that they show LC phase behaviour only in mixtures with other compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are polymerised.

The terms 'polymerisable' and 'reactive' refer to compounds or groups that are capable of participating in a polymerisation reaction, like radicalic or ionic chain polymerisation, polyaddition or polycondensation, and reactive compounds or reactive groups that are capable of being grafted for example by condensation or addition to a polymer backbone in a polymeranalogous reaction. The terms 'non-polymerisable' and 'non-reactive' refer to compounds that do not have 'polymerisable' or 'reactive' groups.

The term 'film' includes self-supporting, i.e., free-standing, films that show more or less pronounced mechanical stability and flexibility, as well as coatings or layers on a supporting substrate or between two substrates.

Detailed Description of the Invention

Especially preferred are compounds, mono-, oligo- and polymers comprising at least one recurring unit of formula I1

35



wherein G and g have the meanings of formula I,

- 5 A is, in case of multiple occurrence independently of one another, $-CX^1=CX^2-$, $-C\equiv C-$, an aromatic or alicyclic ring or a group comprising two or more fused aromatic or alicyclic rings, wherein these rings optionally contain one or more hetero atoms selected from N, O and S, and are
10 optionally mono- or polysubstituted by R^3 as defined in formula I,

X^1 and X^2 are independently of each other H, F, Cl or CN,

- 15 a is, in case of multiple occurrence independently of one another, 0 or 1,

z is an integer ≥ 1 ,

- 20 wherein in case of multiple occurrence the groups $[(G)_g-(A)_a]$ can be identical or different.

Very preferred are compounds, mono-, oligo- and polymers of formula I1A



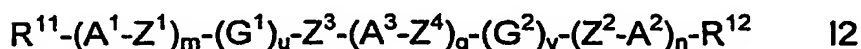
wherein G, g, A, a and z have the meanings of formula I1,

- 30 R^1 and R^2 have independently of each other one of the meanings of R^3 in formula I, or denote $B(OR')(OR'')$ or $SnR^0R^{00}R^{000}$,

- 35 R^{0-000} are independently of each other H or alkyl with 1 to 12 C-atoms,

R' and R" are independently of each other H or alkyl with 1 to 12 C-atoms, or OR' and OR" together with the boron atom may also form a cyclic group having 2 to 10 C atoms.

5 Further preferred are compounds or monomers of formula I2



wherein

10

G¹ and G² have independently of each other one of the meanings of G in formula I,

15

R¹¹ and R¹² have independently of each other one of the meanings of R³ in formula I,

A¹ to A³ have independently of each other one of the meanings of A in formula I1,

20

Z¹ to Z⁴ are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -S-CO-, -CO-S-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CR⁰-, -CY¹=CY²-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

25

Y¹ and Y² are independently of each other H, F, Cl or CN,

R⁰ and R⁰⁰ have the meanings given in formula I,

30

m, n and q are independently of each other 0, 1, 2 or 3,

u and v are independently of each other 0, 1 or 2, with u+v > 0.

35

The compounds, mono-, oligo- and polymers according to the present invention are especially useful as charge transport

semiconductors in that they have high carrier mobilities. Particularly preferred are mono-, oligo- and polymers wherein the group G is substituted by one or more alkyl or fluoroalkyl groups. The introduction of alkyl and fluoroalkyl side chains to the group G improves the solubility and therefore the solution processability of the inventive materials. Furthermore, the presence of fluoroalkyl side chains also renders the inventive materials effective as *n*-type semiconductors. The electron-withdrawing nature of the fluoroalkyl substituents will also lower the HOMO further and result in a more stable material, which is less susceptible to oxidation

Particularly preferred are compounds, mono-, oligo- and polymers comprising at least one group G and at least one reactive group that is capable of a polymerisation or crosslinking reaction.

Further preferred are compounds, mono-, oligo- and polymers comprising at least one group G that are mesogenic or liquid crystalline, in particular polymers of formula I1A forming calamitic phases, and compounds or reactive mesogens of formula I2 forming calamitic phases.

In the oligo- and polymers of the present invention the recurring units $[(G)_g-(A)_a]$ in case of multiple occurrence can be selected of formula I1 independently of each other, so that an oligo- or polymer may comprise identical or different recurring units $[(G)_g-(A)_a]$. The oligo- and polymers thus include homopolymers and copolymers like for example

- statistically random copolymers, for example with a monomer sequence such as -G-A-G-G-A-G-A-A-A-,
- alternating copolymers, for example with a monomer sequence such as -G-A-G-A-G-A-,
- block copolymers, for example with a monomer sequence such as -A-A-G-G-G-G-A-A-A-G-G-G-, and
- homopolymers -G-G-G-G-,

wherein the groups G and A preferably together form a conjugated system.

5 Further preferred are mono-, oligo- and polymers comprising one or more recurring units $[(G)_g-(A)_a]$, wherein $g = 1$ and $a = 0$, very preferably consisting exclusively of such recurring units.

10 Further preferred are mono-, oligo- and polymers comprising one or more recurring units $[(G)_g-(A)_a]$, wherein $g = a = 1$, very preferably consisting exclusively of such recurring units.

The novel compounds have the following advantages

- 15 - they are easy to prepare in excellent yield from cheap, commercially available starting materials,
- they are rod-shaped and suitable as components of LC mixtures in LCDs. They do not necessarily have to exhibit an LC phase themselves, but by being rod-shaped they do not diminish the LC properties of an LC host in which they are dissolved,
- 20 - they can be polymerised if appropriately substituted,
- they pack in a very efficient manner and produce very efficient charge transport, thus making them good candidate materials for OFET use,
- 25 - the anthracene moiety is highly fluorescent on irradiation with UV light, both as a solution and as a thin solid film, and is in particularly suitable for materials emitting blue light,
- potential electroluminescent dopants for eLCD application can be synthesised to have nematic phases, moderate melting points
- 30 and good solubility in nematic LC host mixtures.

Anthracene is particularly good as an emissive LC core, due to the extent of π electron delocalisation across the rings.

In particular the lateral disubstitution of the anthracene core in the compounds of the present invention leads to a number of advantageous properties, like for example the following:

- In prior art it has been reported that in 2,6- substituted anthracenyl LC materials the central positions of the anthracene ring are susceptible to photo dimerisation in a 2+2 cycloaddition reaction (Mery et. al. J. Mat. Chem., 2003, 13, 1622 - 1630). In contrast, in the compounds of the present invention a "capping" substituent is placed on each of the vulnerable 9- and 10-positions, which blocks any photodimerisation reaction and improves material stability.
- In an extended polyaromatic core like that of the compounds of formula I2, comprising the anthracene group plus one or more ring groups A^{1-3} , the use of long chain substituents R^5 to R^{10} on the anthracene core has a disrupting effect on the crystalline packing of cores. This reduces the melting point and promotes nematic phases. This is especially beneficial for electroluminescence, where close crystalline packing of aromatic cores can promote quenching and excimer emission at longer wavelengths. Additionally, if the lateral substituents are chosen correctly, tuning of the electroluminescence wavelength is possible.

The preferred field of use of materials according to the present invention is as semiconductor or charge transport or as light-emitting material, or as a component of such materials. These materials can be used in electronic devices like for example OFETs as components of ICs, as TFTs in flat panel display applications or for RFID tags, or in semiconducting or light-emitting components for OLED applications, electroluminescent displays or backlights of LCDs, for photovoltaic or sensor devices.

Another aspect of the invention relates to polymerisable compounds, in particular those of formula I2, also known as reactive mesogens (RM), and to LC polymers obtained from these compounds or mixtures comprising them.

Especially suitable polymerisable compounds, in particular for semiconductor and light-emitting applications, are those having polymerisable groups P selected from vinyl ether and propenyl ether, as these are linear photopolymerisable groups. These
5 compounds have improved mesogenicity and reduced flow viscosity, both of which are desirable for processing of the materials for use in devices, specifically by reducing the time required for self alignment of the molecules in LC phases compared to other RM polymerisable groups, such as acrylates and to LC polymer materials.

10 Another aspect of the invention relates to highly ordered anisotropic LC polymer films that are obtained from polymerisable compounds or reactive mesogens of the present invention, in particular those of formula I2, or mixtures comprising them, by aligning them in their LC
15 phase into uniform orientation and polymerising them in situ, e.g. by thermal or photopolymerisation.

The compounds of the present invention can also be used in mixtures for LCD applications, in particular for applications using LC mixtures in
20 the nematic or isotropic phase where high birefringence is required.

Furthermore, the compounds of the present invention can be used as reactive mesogens to make polymers or polymer films for use as optical films, in particular optical retardation or compensation films,
25 alignment layers, colour filters or polarisers in an LCD.

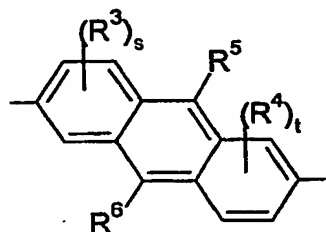
It is also possible to co-polymerise compounds of the present invention via group P with other polymerisable mesogenic or LC monomers, and/or with other compounds of the present invention, in
30 order to induce or enhance LC phase behaviour.

The LCDs according to the present invention are for example conventional LCDs, in particular those of the DAP (deformation of aligned phases) or VA (vertically aligned) mode, like e.g. ECB
35 (electrically controlled birefringence), CSH (colour super homeotropic), VAN or VAC (vertically aligned nematic or cholesteric)

displays, MVA (multi-domain vertically aligned) or PVA (patterned vertically aligned) displays, in displays of the bend mode or hybrid type displays, like e.g. OCB (optically compensated bend cell or optically compensated birefringence), R-OCB (reflective OCB), HAN (hybrid aligned nematic) or pi-cell (π -cell) displays, furthermore in displays of the TN (twisted nematic), HTN (highly twisted nematic) or STN (super twisted nematic), in AMD-TN (active matrix driven TN) displays, in displays of the IPS (in plane switching) mode which are also known as 'super TFT' displays, in displays using liquid crystals in the isotropic state, hereinafter shortly referred to as "isotropic mode display", as described for example in DE 102 172 73 and WO 02/93244 A1, or in bistable nematic displays.

Particularly preferred compounds, mono-, oligo- and polymers of formula I, I1, I1A and I2 are those wherein

- G is of a group of the formula



- z is an integer from 1 to 5000,
- z is an integer from 2 to 5000, in particular from 20 to 1000,
- z is an integer from 2 to 5,
- z is 2 and one or both of R^1 and R^2 denote P-Sp-,
- z is an integer from 1 to 15 and one or both of R^1 and R^2 denote P-Sp-,
- z is an integer from 2 to 5000 and R^1 and R^2 are not P-Sp-,
- the molecular weight is from 5000 to 100000,
- A or A^{1-3} denote optionally substituted arylene or heteroarylene,
- A or A^{1-3} denote $-CX^1=CX^2-$ or $-C\equiv C-$,

- in at least one recurring unit $[(G)_g-(A)_a]$ $g = a = 1$,
- Z^{1-4} are selected from $-O-$, $-CH=CR^0-$, $-CY^1=CY^2-$, $-C\equiv C-$, or a single bond, most preferably $-CH=CH-$, $-C\equiv C-$ or a single bond
- 5 - at least one of Z^{1-4} , preferably Z^1 and Z^2 , especially all of Z^{1-4} denote a single bond,
- A or A^{1-3} denote 1,4-phenylene that is optionally substituted by one or more groups R^3 , in particular 1,4-phenylene substituted by one or two fluorine atoms.
- 10 - one or both of R^1 and R^2 denote P-Sp-,
- R^3 and R^4 are selected from F, Cl, CN, alkyl, oxaalkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl with 1 to 15 C-atoms or alkenyl, alkenyloxy or alkynyl with 2 to 15 C-atoms,
- 15 - Sp is alkylene with 2 to 12 C atoms which is optionally mono- or polysubstituted by F and wherein one or more non-adjacent CH_2 may be replaced, in each case independently from one another, by $-O-$, $-CH=CH-$ or $-C\equiv C-$, preferably $-(CH_2)_u-$ wherein u is an integer from 1 to 6,
- 20 - Sp is linked to A^{1-3} via a group selected from $-O-$, $-COO-$, $-OCO-$, $-OCOO-$ and a single bond.
- Sp is single bond,
- m and n are 1,
- 25 - m is 1 and n is 0 or 1,
- m and n are 2,
- s and/or t are 0,
- s and/or t is 1 or 2,
- 30 - u is 1 and v is 1,
- v is 0 and q is 0,
- $u = v = q = 1$,
- 35 - R^{5-10} are selected from F, Cl, CN, C_1 - C_{20} -alkyl that is optionally substituted with one or more fluorine atoms, C_1 - C_{20} -alkenyl, C_1 -

C₂₀-alkynyl, C₁-C₂₀-alkoxy, C₁-C₂₀-thioalkyl, C₁-C₂₀-silyl, C₁-C₂₀-ester, C₁-C₂₀-amino, C₁-C₂₀-fluoroalkyl, (CH₂CH₂O)_m with m being an integer from 1 to 6, very preferably C₁-C₂₀-alkyl C₁-C₂₀-alkoxy, C₁-C₂₀-thioalkyl or C₁-C₂₀-fluoroalkyl,

5

A and A¹⁻³ are independently of each other an aromatic or alicyclic ring, preferably a 5-, 6- or 7-membered ring, or a group comprising two or more, preferably two or three, fused aromatic or alicyclic rings, wherein these rings optionally contain one or more hetero atoms selected from N, O and S, and are optionally mono- or polysubstituted with R³ as defined above.

10

R³ and R⁴ are preferably F, Cl, CN, OH, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, OCF₃, OCHF₂ or OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ or OCF₃, most preferably F, Cl, CH₃, OCH₃ or COCH₃.

15

Preferred groups A and A¹⁻³ are for example furan, pyrrol, thiophene, oxazole, thiazole, thiadiazole, imidazole, phenylene, cyclohexylene, cyclohexenylene, pyridine, pyrimidine, pyrazine, azulene, indane, naphthalene, tetrahydronaphthalene, anthracene and phenanthrene.

20

Particularly preferably A and A¹⁻³ are selected from furane-2,5-diyl, thiophene-2,5-diyl, thienothiophene-2,5-diyl, dithienothiophene-2,6-diyl, pyrrol-2,5-diyl, 1,4-phenylene, azulene-2,6-diyl, pyridine-2,5-diyl, pyrimidine-2,5-diyl, naphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl, indane-2,5-diyl, or 1,4-cyclohexylene wherein one or two non-adjacent CH₂ groups are optionally replaced by O and/or S, wherein these groups are unsubstituted, mono- or polysubstituted by R³ as defined above.

25

30

Preferably the groups (A¹-Z¹)_m and (Z²-A²)_n and (A³-Z⁴)_q contain only monocyclic groups A¹⁻³. Very preferably the groups (A¹-Z¹)_m and (Z²-A²)_n and (A³-Z⁴)_q comprise one or two 5- or 6-membered rings.

35

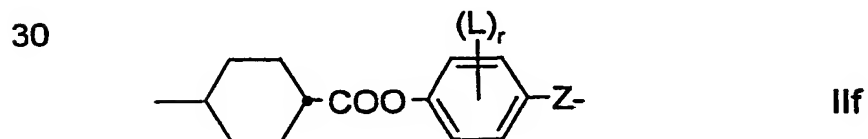
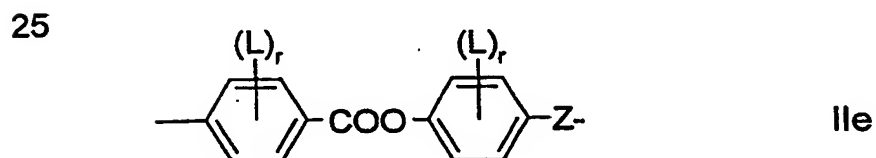
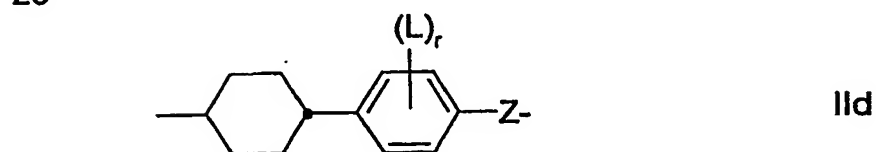
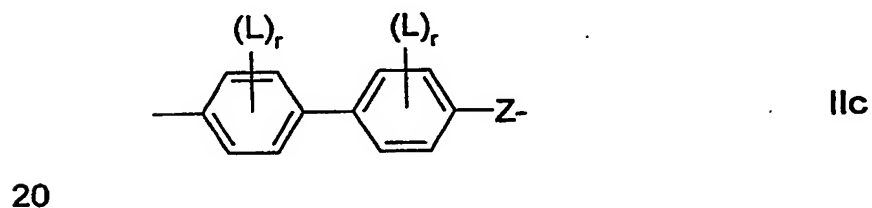
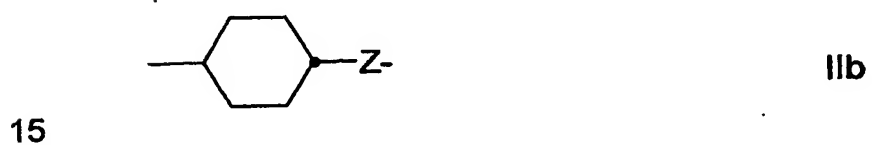
The groups $(A^1-Z^1)_m$ and $(Z^2-A^2)_n$ and $(A^3-Z^4)_q$ can be identical or different. In a preferred embodiment of the present invention the groups $(A^1-Z^1)_m$ and $(Z^2-A^2)_n$ are mirror images of each other, and very preferably the group $(A^1-Z^1)_m-(G^1)_u-Z^3-(A^3-Z^4)_q-(G^2)_v-(Z^2-A^2)_n$ is a symmetric group. In another preferred embodiment of the present invention the groups $(A^1-Z^1)_m$ and $(Z^2-A^2)_n$ and $(A^3-Z^4)_q$ are different.

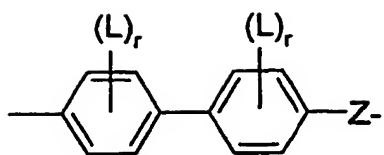
Preferred subformulae for the groups $(A^1-Z^1)_m$ and $(Z^2-A^2)_n$ and $(A^3-Z^4)_q$ are listed below. For reasons of simplicity, Phe in these groups is 1,4-phenylene, PheL is a 1,4-phenylene group which is substituted by 1 to 4 groups L, wherein L has one of the meanings of R^3 as defined above, Pyd is pyridine-2,5-diyl and Pyr is pyrimidine-2,5-diyl. The following list of preferred groups does also comprise the mirror images of the subformulae shown

15	-Phe-Z-	II-1
	-Pyd-Z-	II-2
	-Pyr-Z-	II-3
	-PheL-Z-	II-4
20	-Cyc-Z-	II-5
	-Phe-Z-Cyc-Z-	II-6
	-Cyc-Z-Cyc-Z-	II-7
	-PheL-Cyc-Z-	II-8
	-Phe-Z-Phe-Z-	II-9
25	-Phe-Z-Pyd-Z-	II-10
	-Pyd-Z-Phe-Z-	II-11
	-Phe-Z-Pyr-Z-	II-12
	-Pyr-Z-Phe-Z-	II-13
	-PheL-Z-Phe-Z-	II-14
30	-PheL-Z-Pyd-Z-	II-15
	-PheL-Z-Pyr-Z-	II-16
	-Pyr-Z-Pyd-Z-	II-17
	-Pyd-Z-Pyd-Z-	II-18
	-Pyr-Z-Pyr-Z-	II-19
35	-PheL-Z-PheL-Z-	II-20

In these preferred groups Z has the meaning of Z^1 as given in formula I. Preferably Z is $-\text{CH}_2\text{CH}_2-$, $-\text{CY}^1=\text{CY}^2-$, $-\text{C}\equiv\text{C}-$ or a single bond.

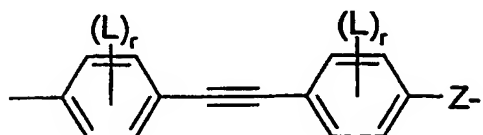
- 5 Very preferably $(A^1-Z^1)_m$ and $(A^3-Z^4)_n$ and $(Z^2-A^2)_n$ are selected from the following formulae and their mirror images





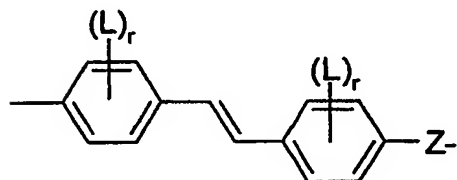
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5



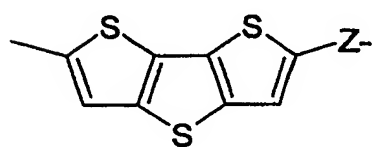
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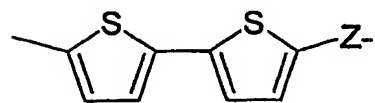
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15



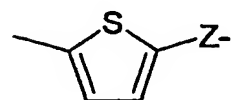
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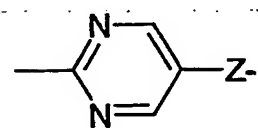


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25

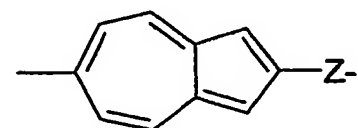


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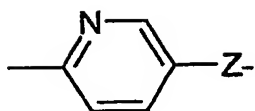
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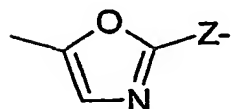


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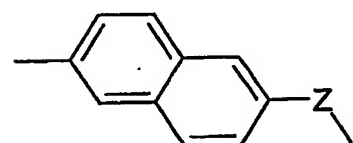
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IIq

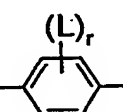
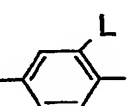
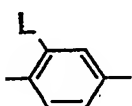
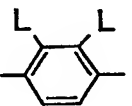
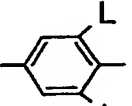


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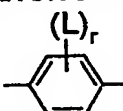
IIss

wherein L has one of the meanings of R^3 given above and r is 0, 1, 2, 3 or 4, preferably 0, 1 or 2.

The group  in these preferred formulae is very preferably denoting , , or , furthermore ,

with L having each independently one of the meanings given above.

Especially preferred compounds comprise at least

one group  wherein r is 1.

Further preferred compounds comprise at least

two groups  wherein r is 1 and/or at least one group

 wherein r is 2.

- Aryl and heteroaryl preferably denote a mono-, bi- or tricyclic aromatic or heteroaromatic with up to 25 C atoms, wherein the rings can be fused, and in which the heteroaromatic groups contain at least one hetero ring atom, preferably selected from N, O and S.
- 5 The aryl and heteroaryl groups are optionally substituted with one or more of F, Cl, Br, I, CN, and straight chain, branched or cyclic alkyl having 1 to 20 C atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I, -CN or -OH, and in which one or more non-adjacent CH₂ groups are optionally replaced, in each case
- 10 independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another.
- 15 Especially preferred aryl and heteroaryl groups are phenyl in which, in addition, one or more CH groups may be replaced by N, naphthalene, thiophene, thienothiophene, dithienothiophene, alkyl fluorene and oxazole, all of which are unsubstituted, mono- or polysubstituted with L, wherein L is halogen or an alkyl, alkoxy,
- 20 alkylcarbonyl or alkoxycarbonyl group with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl.
- Arylene and heteroarylene preferably denote a mono-, bi- or tricyclic divalent aromatic or heteroaromatic radicals with up to 25 C atoms,
- 25 wherein the rings can be fused, and in which the heteroaromatic groups contain at least one hetero ring atom, preferably selected from N, O and S. The arylene and heteroarylene groups are optionally substituted with one or more of F, Cl, Br, I, CN, and straight chain, branched or cyclic alkyl having 1 to 20 C atoms, which
- 30 is unsubstituted, mono- or poly-substituted by F, Cl, Br, I, -CN or -OH, and in which one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S
- 35 atoms are not linked directly to one another.

Especially preferred arylene and heteroarylene groups are 1,4-phenylene in which, in addition, one or more CH groups are optionally replaced by N, naphthalene-2,6-diyl, thiophene-2,5-diyl, thienothiophene-2,5-diyl, dithienothiophene-2,6-diyl, alkyl fluorene and oxazole, all of which are unsubstituted, mono- or polysubstituted with L as defined above.

$CX^1=CX^2$ is preferably -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF-, -CH=C(CN)- or -C(CN)=CH-.

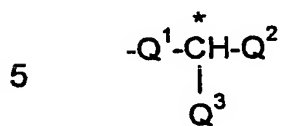
If one of R^{1-10} is an alkyl or alkoxy radical, i.e. where the terminal CH_2 group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

Oxaalkyl, i.e. where one CH_2 group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

If one of R^{1-10} is an alkyl group wherein one or more CH_2 groups are replaced by -CH=CH-, this may be straight-chain or branched. It is preferably straight-chain, has 2 to 10 C atoms and accordingly is preferably vinyl, prop-1-, or prop-2-enyl, but-1-, 2- or but-3-enyl, pent-1-, 2-, 3- or pent-4-enyl, hex-1-, 2-, 3-, 4- or hex-5-enyl, hept-1-, 2-, 3-, 4-, 5- or hept-6-enyl, oct-1-, 2-, 3-, 4-, 5-, 6- or oct-7-enyl, non-1-, 2-, 3-, 4-, 5-, 6-, 7- or non-8-enyl, dec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or dec-9-enyl.

- Especially preferred alkenyl groups are C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl, C₅-C₇-4-alkenyl, C₆-C₇-5-alkenyl and C₇-6-alkenyl, in particular C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl and C₅-C₇-4-alkenyl. Examples for particularly preferred alkenyl groups are vinyl,
- 5 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 C atoms are generally preferred.
- 10 If one of R¹⁻¹⁰ is an alkyl or alkenyl group that is monosubstituted by CN or CF₃, it is preferably straight-chain. The substitution by CN or CF₃ can be in any desired position.
- 15 If one of R¹⁻¹⁰ is an alkyl or alkenyl group that is at least monosubstituted by halogen, it is preferably straight-chain. Halogen is preferably F or Cl, in case of multiple substitution preferably F. The resulting groups include also perfluorinated groups. In case of monosubstitution the F or Cl substituent can be in any desired position, but is preferably in ω-position. Examples for especially
- 20 preferred straight-chain groups with a terminal F substituent are fluormethyl, 2-fluorethyl, 3-fluorpropyl, 4-fluorbutyl, 5-fluorpentyl, 6-fluorhexyl and 7-fluorheptyl. Other positions of F are, however, not excluded.
- 25 Halogen is preferably F or Cl.
-
- 30 R¹⁻¹⁰ can be a polar or a non-polar group. In case of a polar group, it is selected from CN, SF₅, halogen, OCH₃, SCN, COR¹¹, COOR¹¹ or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms. R¹¹ is optionally fluorinated alkyl with 1 to 4, preferably 1 to 3 C atoms. Especially preferred polar groups are selected of F, Cl, CN, OCH₃, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, CHF₂, CH₂F, OCF₃, OCHF₂, OCH₂F, C₂F₅ and OC₂F₅, in particular F, Cl, CN, CF₃, OCHF₂ and OCF₃. In case of a non-polar group, it is preferably alkyl
- 35 with up to 15 C atoms or alkoxy with 2 to 15 C atoms.

R^{1-10} can be an achiral or a chiral group. In case of a chiral group it is preferably selected of formula III:



III

wherein

10 Q^1 is alkylene or alkylene-oxy with 1 to 9 C atoms, arylene or heteroarylene as defined above, or a single bond,

15 Q^2 is alkyl or alkoxy with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by F, Cl, Br or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by $-\text{C}\equiv\text{C}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{CH}_3)-$, $-\text{CO}-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{OCO-O}-$, $-\text{S-CO}-$ or $-\text{CO-S}-$ in such a manner that oxygen atoms are not linked directly to one another, or aryl or heteroaryl as defined above, being different from Q^1 or Q^3 ,

20

Q^3 is F, Cl, Br, CN or alkyl, alkoxy, aryl or heteroaryl as defined for Q^2 but being different from Q^2 or Q^1 ,

25 In case Q^1 in formula III is an alkylene-oxy group, the O atom is preferably adjacent to the chiral C atom.

Preferred chiral groups of formula III are 2-alkyl, 2-alkoxy, 2-methylalkyl, 2-methylalkoxy, 2-fluoroalkyl, 2-fluoroalkoxy, 2-(2-ethin)-alkyl, 2-(2-ethin)-alkoxy, 1,1,1-trifluoro-2-alkyl and 1,1,1-trifluoro-2-alkoxy.

30

Particularly preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl,

35


2-hexyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, 1,1,1-trifluoro-2-octyloxy, 1,1,1-trifluoro-2-octyl, 2-fluoromethyloctyloxy for example. Very preferred are 2-hexyl, 2-octyl, 2-octyloxy, 1,1,1-trifluoro-2-hexyl, 1,1,1-trifluoro-2-octyl and 1,1,1-trifluoro-2-octyloxy.

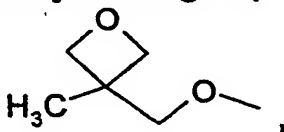
In addition, compounds containing an achiral branched group R^{1-10} may occasionally be of importance, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

The polymerisable or reactive group P is preferably selected from

$CH_2=CW^1-COO-$, $W^2HC-\text{CH}_2-\text{CH}-$, $W^2-\text{CH}(\text{CH}_2)_{k_1}-O-$, $CH_2=CW^2-(O)_{k_1}-$, $CH_3-CH=CH-O-$, $(CH_2=CH)_2CH-OCO-$, $(CH_2=CH-CH_2)_2CH-OCO-$, $(CH_2=CH)_2CH-O-$, $(CH_2=CH-CH_2)_2N-$, $HO-CW^2W^3-$, $HS-CW^2W^3-$, HW^2N- , $HO-CW^2W^3-NH-$, $CH_2=CW^1-CO-NH-$, $CH_2=CH-(COO)_{k_1}-Phe-(O)_{k_2}-$, $Phe-CH=CH-$, $HOOC-$, $OCN-$, and $W^4W^5W^6Si-$, with W^1 being H, Cl, CN, phenyl or alkyl with 1 to 5 C-atoms, in particular H, Cl or CH_3 , W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular H, methyl, ethyl or n-propyl, W^4 , W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene and k_1 and k_2 being independently of each other 0 or 1.

Especially preferably P is a group without a carbonyl moiety,

preferably selected from W^2  $(CH_2)_{k1}-O-$, $CH_2=CW^2-(O)_{k1}-$ and $CH_3-CH=CH-O-$ as defined above, very preferably a vinyl group $CH_2=CH-$, a vinyl ether group $CH_2=CH-O-$, a propenyl ether group

$CH_3-CH=CH-O-$ or an oxetane group of formula , most preferably a vinyl ether group.

As for the spacer group Sp all groups can be used that are known for this purpose to the skilled in the art. The spacer group Sp is preferably of formula $Sp'-X$, such that $P-Sp-$ is $P-Sp'-X-$, wherein

Sp' is alkylene with up to 30 C atoms which is unsubstituted or mono- or polysubstituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by $-O-$, $-S-$, $-NH-$, $-NR^0-$, $-SiR^0R^{00}-$, $-CO-$, $-COO-$, $-OCO-$, $-OCO-O-$, $-SCO-$, $-CO-S-$, $-CH=CH-$ or $-C\equiv C-$ in such a manner that O and/or S atoms are not linked directly to one another,

X is $-O-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-O-COO-$, $-CO-NR^0-$, $-NR^0-CO-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, $-CH=N-$, $-N=CH-$, $-N=N-$, $-CH=CR^0-$, $-CY^1=CY^2-$, $-C\equiv C-$, $-CH=CH-COO-$, $-OCO-CH=CH-$ or a single bond, and

R^0 , R^{00} , Y^1 and Y^2 have one of the meanings given above.

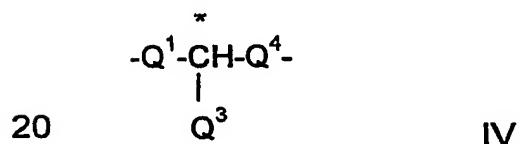
X is preferably $-O-$, $-S-$, $-OCH_2-$, $-CH_2O-$, $-SCH_2-$, $-CH_2S-$, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2CH_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CF_2CF_2-$, $-CH=N-$, $-N=CH-$, $-N=N-$, $-CH=CR^0-$, $-CX^1=CX^2-$, $-C\equiv C-$ or a single bond, in particular $-O-$, $-S-$, $-C\equiv C-$, $-CX^1=CX^2-$ or a single bond. In

another preferred embodiment X is a group that is able to form a conjugated system, such as $-C\equiv C-$ or $-CX^1=CX^2-$, or a single bond.

5 Typical groups Sp' are, for example, $-(CH_2)_p-$, $-(CH_2CH_2O)_q-CH_2CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$ or $-CH_2CH_2-NH-CH_2CH_2-$ or $-(SiR^0R^{00}-O)_p-$, with p being an integer from 2 to 12, q being an integer from 1 to 3 and R^0 and R^{00} having the meanings given above.

10 Preferred groups Sp' are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene for example.

15 In another preferred embodiment Sp' is a chiral group of formula IV:



wherein

25 Q^1 and Q^3 have the meanings given in formula III, and

Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1 ,

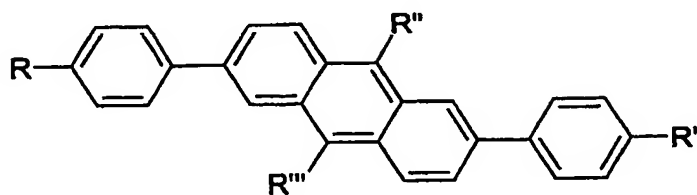
30 with Q^1 being linked to the polymerizable group P.

Further preferred are compounds with one or two groups P-Sp- wherein Sp is a single bond.

35 In case of compounds with two groups P-Sp, each of the two polymerisable groups P and the two spacer groups Sp can be identical or different.

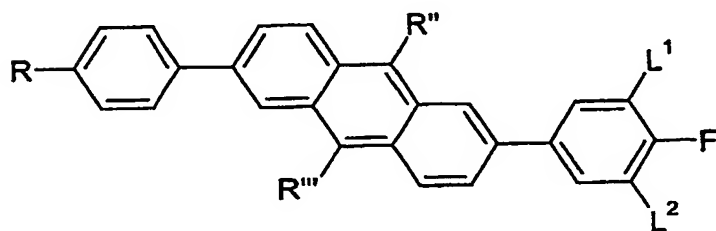
Particularly preferred compounds of formula 12 are those of the following formulae

5



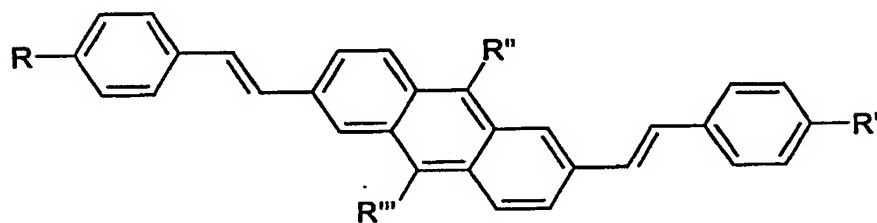
1a

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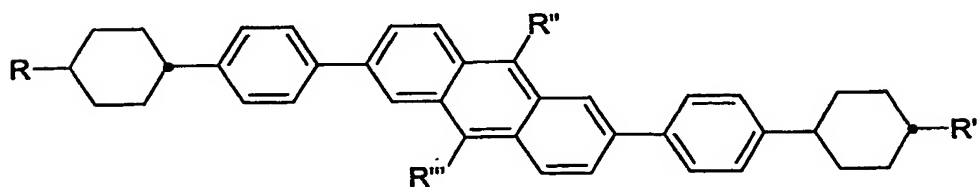
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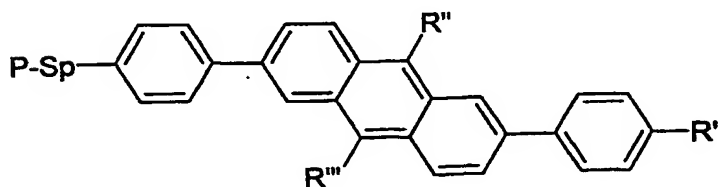
1c

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1d

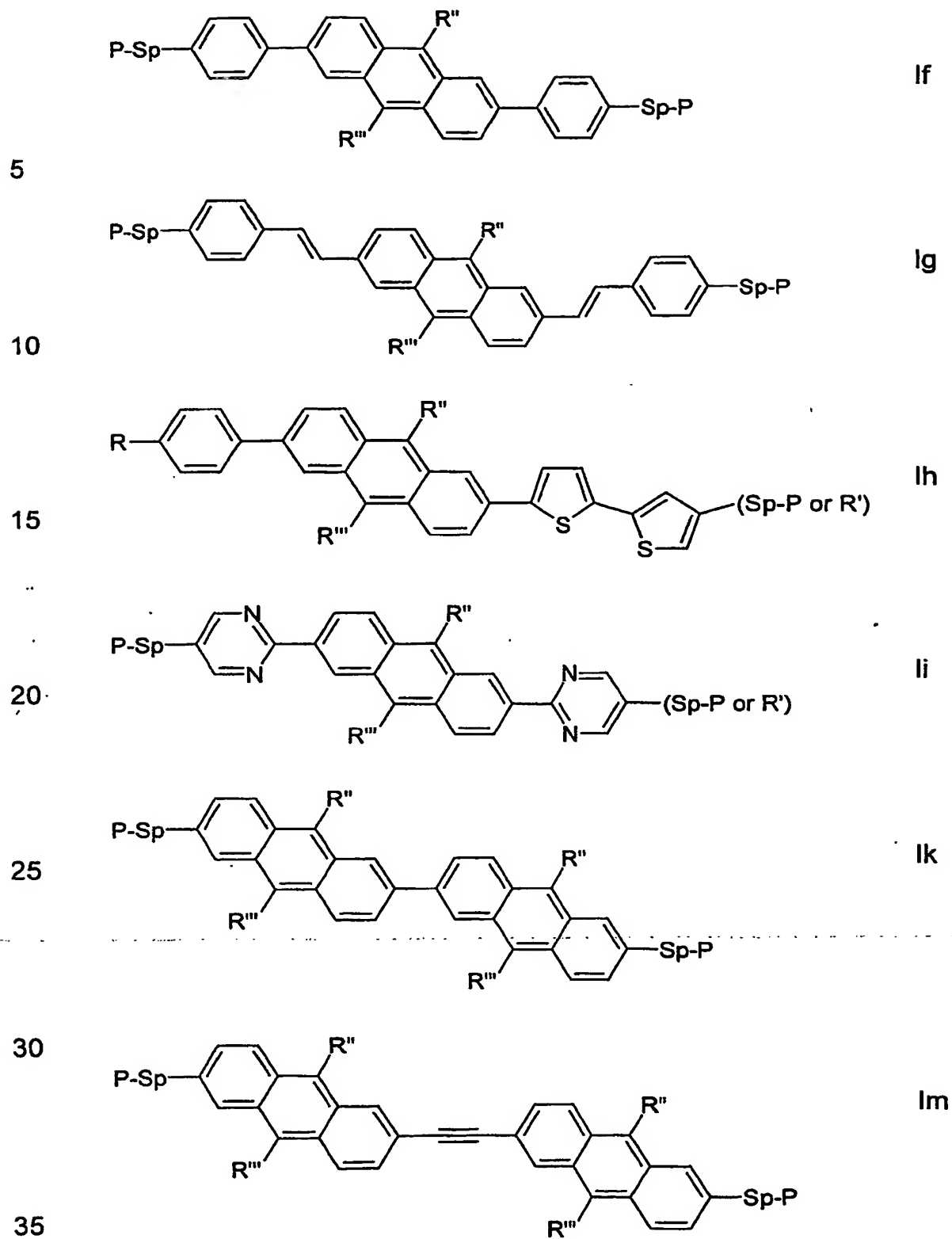
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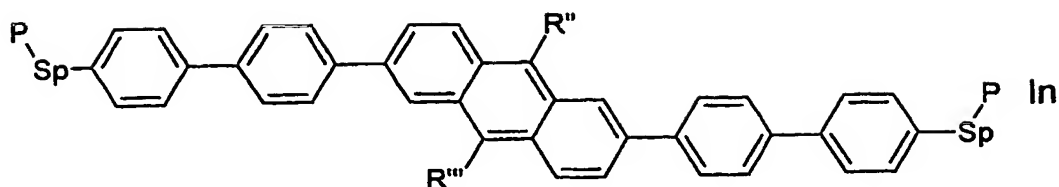


1e

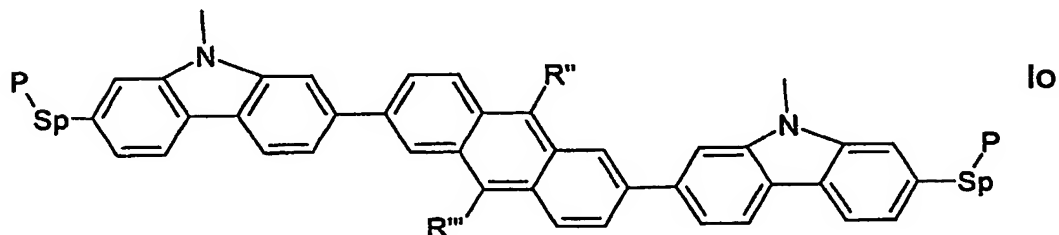
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5



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wherein

15 R and R' have independently of each other one of the meanings of R¹ in formula I and are preferably straight chain alkyl or alkoxy with 1 to 12 C-atoms or alkenyl, alkenyloxy or alkynyl with 2 to 12 C-atoms,

20 R'' and R''' have independently of each other one of the meanings of R⁵ in formula I and are preferably straight chain alkyl, alkoxy, thioalkyl or fluorinated alkyl with 1 to 20 C-atoms, very preferably with 5 to 15 C-atoms,

25 P and Sp have the meanings given above and below, and

L¹ and L² are independently of each other H or F.

30 The aromatic rings in the above preferred formulae are optionally substituted with 1, 2 or 3 groups R³ as defined above.

35 Particularly preferred oligo- and polymers of formula I1 or I1A are those comprising a recurring unit selected from the above preferred formulae Ia to Im (without the terminal groups R or P-Sp), wherein z is an integer from 2 to 5000, in particular from 20 to 1000, Ar is 1,4-phenylene, 2,6-naphthalene, alkoxyphenylene, alkylfluorene,

thiophene-2,5-diyl, thienothiophene-2,5-diyl or dithienothiophene-2,6-diyl, X^1 and X^2 are H, CN or F, and wherein R^4 and R^5 are independently of each other H, halogen, alkyl with 1-16 C atoms that is optionally fluorinated, or P-Sp-.

5

SCLCPs obtained from the inventive compounds or mixtures by polymerisation or copolymerisation have a backbone that is formed by the polymerisable group P.

10

The compounds according to the present invention can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Some specific and preferred methods are described in the reaction schemes below. Further methods can be taken from the examples.

15

20

The LC media according to the present invention preferably contain at least one compound of the present invention, very preferably of formula I2, and a nematic host mixture comprising one or more nematic or nematogenic compounds.

25

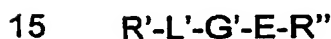
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35

Preferably the LC media consist of 2 to 25, preferably 3 to 15 compounds, at least one of which is a compound of formula I. The other compounds forming the nematic host mixture are preferably low molecular weight liquid crystal compounds selected from nematic or nematogenic substances, for example from the known classes of the azoxybenzenes, benzylidene-anilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl esters of cyclohexanecarboxylic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylcyclohexanecarboxylic acid, cyclohexylphenyl esters of benzoic acid, of cyclohexanecarboxylic acid and of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-

cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexylpyridazines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenyl-ethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)-ethanes, 1-cyclohexyl-2-biphenyl-ethanes, 1-phenyl-2-cyclohexyl-phenylethanes, optionally halogenated stilbenes, benzyl phenyl ether, tolanes, substituted cinnamic acids and further classes of nematic or nematogenic substances. The 1,4-phenylene groups in these compounds may also be laterally mono- or difluorinated.

The most important compounds that are possible as components of these LC mixtures can be characterized by the following formula



wherein L' and E, which may be identical or different, are in each case, independently from one another, a bivalent radical from the group formed by -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -B-Phe- and -B-Cyc- and their mirror images, where Phe is unsubstituted or fluorine-substituted 1,4-phenylene, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and B is 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

G' in these compounds is selected from the following bivalent groups -CH=CH-, -N(O)N-, -CH=CY-, -CH=N(O)-, -C≡C-, -CH₂-CH₂-, -CO-O-, -CH₂-O-, -CO-S-, -CH₂-S-, -CH=N-, -COO-Phe-COO- or a single bond, with Y being halogen, preferably chlorine, or -CN.

R' and R'' are, in each case, independently of one another, alkyl, alkenyl, alkoxy, alkenyloxy, alkanoyloxy, alkoxycarbonyl or alkoxycarbonyloxy with 1 to 18, preferably 3 to 12 C atoms, or alternatively one of R' and R'' is F, CF₃, OCF₃, Cl, NCS or CN.

In most of these compounds R' and R'' are, in each case, independently of each another, alkyl, alkenyl or alkoxy with different chain length, wherein the sum of C atoms in nematic media generally is between 2 and 9, preferably between 2 and 7.

5

Many of these compounds or mixtures thereof are commercially available. All of these compounds are either known or can be prepared by methods which are known per se, as described in the literature (for example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for said reactions. Use may also be made here of variants which are known per se, but are not mentioned here.

10

15

Another aspect of the present invention relates to compounds of the present invention that comprise one or more polymerisable groups. Very preferred materials of this type are monomers of formula I2 wherein R¹ and/or R² denote P-Sp-.

20

Another aspect of the invention relates to a polymerisable LC material comprising one or more compounds of the present invention and optionally comprising one or more polymerisable compounds.

25

Another aspect of the present invention relates to an anisotropic polymer film obtainable from a polymerisable LC material as defined above that is aligned in its LC phase into macroscopically uniform orientation and polymerised or crosslinked to fix the oriented state.

30

The polymerisable compounds and mixtures according to the present invention are particularly useful as semiconductor, charge transport or light-emitting materials, as they can be aligned into uniform highly ordered orientation in their LC phase by known techniques, thus exhibiting a higher degree of order that leads to particularly high charge carrier mobility. The highly ordered LC state can be fixed by

35

in situ polymerisation or crosslinking via the groups P to yield

polymer films with high charge carrier mobility and high thermal, mechanical and chemical stability. The materials also emit light on the application of an electric field at a range of wavelengths, dependent on the exact molecular substitution. Additionally, the highly ordered LC state fixated in the anisotropic polymer film will give rise to an anisotropy of electroluminescence, with polarisation of that anisotropy corresponding to the long molecular axis of LC orientation.

10 The materials according to the present invention are ideally solution processable and are suitable as part of an OFET or OLED device in conjunction with hole and electron transport layers and suitable workfunction electrode structures.

15 For example, an OLED or OFET component can be made by in-situ polymerisation of a polymerisable LC material comprising one or more compounds of formula I2, wherein one or both of R^1 and R^2 denote P-Sp-. If an LC polymer is prepared first, for example by polymerisation in solution, and the isolated LC polymer is used to make the device, said LC polymer is preferably made from an LC material comprising one or more compounds of formula I wherein one of R^1 and R^2 denote P-Sp-.

20 Particularly preferred are LC materials having a nematic and/or smectic phase. For OFET applications smectic materials are especially preferred. For OLED applications nematic, chiral nematic or smectic materials are especially preferred.

30 It is also possible to copolymerise the polymerisable compounds or mixtures according to the present invention with other mesogenic or LC monomers that are known from prior art, in order to induce or enhance LC phase behaviour. Polymerisable mesogenic compounds that are suitable as comonomers are known in prior art and disclosed for example in WO 93/22397, EP 0 261 712, DE 195 04 224, WO 35 95/22586, WO 97/00600 and GB 2 351 734. The compounds

disclosed in these documents, however, are to be regarded merely as examples that shall not limit the scope of this invention.

5 Preferably the polymerisable LC mixture comprises at least one polymerisable mesogenic compound having one polymerisable functional group and at least one polymerisable mesogenic compound having two or more polymerisable functional groups.

10 The polymerisable LC mixtures according to the present invention may also comprise one or more non-reactive chiral dopants or chiral polymerisable mesogenic compounds. Typically used chiral dopants are e.g. the commercially available R or S 811, R or S 1011, R or S 2011 or CB 15 (from Merck KGaA, Darmstadt, Germany). Very
15 preferred are chiral compounds with a high helical twisting power (HTP), in particular compounds comprising a sorbitol group as described in WO 98/00428, compounds comprising a hydrobenzoin group as described in GB 2,328,207, chiral binaphthyl derivatives as described in WO 02/94805, chiral binaphthol acetal derivatives as described in WO 02/34739, chiral TADDOL derivatives as described
20 in WO 02/06265, and chiral dopants with at least one fluorinated linkage group and a terminal or central chiral group as described in WO 02/06196 and WO 02/06195.

25 Preferably polymerisation is carried out as in-situ polymerisation of a coated layer of the material, preferably during fabrication of the electronic or optical device comprising the inventive semiconductor or light-emitting material.

30 In case of OFET manufacture, the LC materials are preferably aligned in their LC state into homeotropic orientation prior to polymerisation, where the conjugated pi-electron systems are orthogonal to the direction of charge transport. This ensures that the intermolecular distances are minimised and hence then energy required to transport charge between molecules is minimised. In
35 case of use in OLED devices or e.g. optical films or alignment layers,

other orientations like planar, tilted or splayed alignment may be preferred.

5 The oriented LC material is then polymerised or crosslinked to fix the uniform orientation of the LC state. Alignment and curing are carried out in the LC phase or mesophase of the material. This technique is known in the art and is generally described for example in D.J. Broer, et al., *Angew. Makromol. Chem.* 183, (1990), 45-66

10 Uniform alignment of the LC material can be achieved for example by treatment of the substrate onto which the material is coated, by shearing the material during or after coating, by application of a magnetic or electric field to the coated material, or by the addition of surface-active compounds to the liquid crystal material. Reviews of
15 alignment techniques are given for example by I. Sage in "Thermotropic Liquid Crystals", edited by G. W. Gray, John Wiley & Sons, 1987, pages 75-77, and by T. Uchida and H. Seki in "Liquid Crystals - Applications and Uses Vol. 3", edited by B. Bahadur, World Scientific Publishing, Singapore 1992, pages 1-63. A review of
20 alignment materials and techniques is given by J. Cognard, *Mol. Cryst. Liq. Cryst.* 78, Supplement 1 (1981), pages 1-77.

Polymerisation takes place by exposure to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or
25 visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. Preferably polymerisation is carried out by UV irradiation at a non-absorbing wavelength. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp
30 power the curing time can be reduced. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

35 Polymerisation is preferably carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For example, when polymerising by means of UV light, a photoinitiator can be used

that decomposes under UV irradiation to produce free radicals or ions that start the polymerisation reaction. When curing for example polymerisable materials with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing for example
5 polymerisable materials with vinyl ether, epoxide and oxetane groups, preferably a cationic photoinitiator is used. It is also possible to use a polymerisation initiator that decomposes when heated to produce free radicals or ions that start the polymerisation. As a photoinitiator for radical polymerisation for example the commercially
10 available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerisation the commercially available UVI 6974 (Union Carbide) can be used.

15 The polymerisable material can additionally comprise one or more other suitable components such as, for example, catalysts, sensitizers, stabilizers, inhibitors, chain-transfer agents, co-reacting monomers, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers,
20 defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes or pigments.

Another aspect of the invention relates to a liquid crystal side chain polymer (SCLCP) obtained from a polymerisable compound or
25 mixture as defined above by polymerisation or polymeranalogous reaction. Particularly preferred are SCLCPs obtained from one or more monomers of formula I2 wherein one or both of R^1 and R^2 are a polymerisable or reactive group, or from a polymerisable mixture comprising one or more of said monomers.

30 Another aspect of the invention relates to an SCLCP obtained from one or more compounds of formula I2 wherein one or both of R^1 and R^2 are a polymerisable group, or from a polymerisable LC mixture as defined above, by copolymerisation or polymer analogous reaction
35 together with one or more additional mesogenic or non-mesogenic comonomers.

Side chain liquid crystal polymers or copolymers (SCLCPs), in which the semiconducting component is located as a pendant group, separated from a flexible backbone by an aliphatic spacer group, offer the possibility to obtain a highly ordered lamellar like morphology. This structure consists of closely packed conjugated aromatic mesogens, in which very close (typically $< 4 \text{ \AA}$) pi-pi stacking can occur. This stacking allows intermolecular charge transport to occur more easily, leading to high charge carrier mobilities. SCLCPs are advantageous for specific applications as they can be readily synthesized before processing and then e.g. be processed from solution in an organic solvent. If SCLCPs are used in solutions, they can orient spontaneously when coated onto an appropriate surface and when at their mesophase temperature, which can result in large area, highly ordered domains.

SCLCPs can be prepared from the polymerisable compounds or mixtures according to the invention by the methods described above, or by conventional polymerisation techniques which are known to those skilled in the art, including for example radicalic, anionic or cationic chain polymerisation, polyaddition or polycondensation. Polymerisation can be carried out for example as polymerisation in solution, without the need of coating and prior alignment, or polymerisation in situ. It is also possible to form SCLCPs by grafting compounds according to the invention with a suitable reactive group, or mixtures thereof, to presynthesized isotropic or anisotropic polymer backbones in a polymer analogous reaction. For example, compounds with a terminal hydroxy group can be attached to polymer backbones with lateral carboxylic acid or ester groups, compounds with terminal isocyanate groups can be added to backbones with free hydroxy groups, compounds with terminal vinyl or vinyloxy groups can be added, e.g., to polysiloxane backbones with Si-H groups. It is also possible to form SCLCPs by copolymerisation or polymer analogous reaction from the inventive compounds together with conventional mesogenic or non mesogenic comonomers. Suitable comonomers are known to those skilled in the

art. In principle it is possible to use all conventional comonomers known in the art that carry a reactive or polymerisable group capable of undergoing the desired polymer-forming reaction, like for example a polymerisable or reactive group P as defined above. Typical mesogenic comonomers are for example those mentioned in WO 93/22397, EP 0 261 712, DE 195 04 224, WO 95/22586, WO 97/00600 and GB 2 351 734. Typical non mesogenic comonomers are for example alkyl mono- or diacrylates or alkyl mono- or dimethacrylates with alkyl groups of 1 to 20 C atoms, like methyl acrylate or methyl methacrylate, trimethylpropane trimethacrylate or pentaerythritol tetraacrylate.

A further aspect of the invention relates to both the oxidised and reduced form of the oligo- and polymers of formula I1 and I1A. Either loss or gain of electrons results in formation of a highly delocalised ionic form, which is of high conductivity. This can occur on exposure to common dopants. Suitable dopants and methods of doping are known to those skilled in the art, e.g., from EP 0 528 662, US 5,198,153 or WO 96/21659.

The doping process typically implies treatment of the semiconductor material with an oxidating or reducing agent in a redox reaction to form delocalised ionic centres in the material, with the corresponding counterions derived from the applied dopants. Suitable doping methods comprise for example exposure to a doping vapor in the atmospheric pressure or at a reduced pressure, electrochemical doping in a solution containing a dopant, bringing a dopant into contact with the semiconductor material to be thermally diffused, and ion-implantation of the dopant into the semiconductor material.

When electrons are used as carriers, suitable dopants are for example halogens (e.g., I₂, Cl₂, Br₂, ICl, ICl₃, IBr and IF), Lewis acids (e.g., PF₅, AsF₅, SbF₅, BF₃, BCl₃, SbCl₅, BBr₃ and SO₃), protonic acids, organic acids, or amino acids (e.g., HF, HCl, HNO₃, H₂SO₄, HClO₄, FSO₃H and ClSO₃H), transition metal compounds (e.g., FeCl₃, FeOCl, Fe(ClO₄)₃, Fe(4-CH₃C₆H₄SO₃)₃, TiCl₄, ZrCl₄, HfCl₄,

NbF₅, NbCl₅, TaCl₅, MoF₅, MoCl₅, WF₅, WCl₆, UF₆ and LnCl₃
 (wherein Ln is a lanthanoid), anions (e.g., Cl⁻, Br⁻, I⁻, I₃⁻, HSO₄⁻, SO₄²⁻,
 NO₃⁻, ClO₄⁻, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₄⁻, Fe(CN)₆³⁻, and anions of
 various sulfonic acids, such as aryl-SO₃⁻). When holes are used as
 carriers, examples of dopants are cations (e.g., H⁺, Li⁺, Na⁺, K⁺, Rb⁺
 and Cs⁺), alkali metals (e.g., Li, Na, K, Rb, and Cs), alkaline-earth
 metals (e.g., Ca, Sr, and Ba), O₂, XeOF₄, (NO₂⁺) (SbF₆⁻), (NO₂⁺)
 (SbCl₆⁻), (NO₂⁺) (BF₄⁻), AgClO₄, H₂IrCl₆, La(NO₃)₃ · 6H₂O,
 FSO₂OOSO₂F, Eu, acetylcholine, R₄N⁺, (R is an alkyl group), R₄P⁺
 (R is an alkyl group), R₆As⁺ (R is an alkyl group), and R₃S⁺ (R is an
 alkyl group).

The conducting form of the compounds and materials of the present
 invention can be used as an organic "metal" in applications, for
 example, but not limited to, charge injection layers and ITO
 planarising layers in organic light emitting diode applications, films for
 flat panel displays and touch screens, antistatic films, printed
 conductive substrates, patterns or tracts in electronic applications
 such as printed circuit boards and condensers.

The compounds, mixtures and polymers of the present invention are
 useful as optical, electronic, semiconductor or light-emitting
 materials, in particular as charge transport materials in OFETs as
 components of ICs, RFID tags or TFTs, and as light-emitting
 materials for OLEDs in electroluminescent display applications or as
 backlight of for example LCDs. Alternatively, they may be used as
 photovoltaics or sensor materials, for electrophotographic recording,
 and for other semiconductor applications.

The compounds, mixtures and polymers according to the invention
 are especially useful as charge transport or semiconductor materials,
 or as components of such materials, that have high carrier mobilities.
 Particularly preferred are materials of formula I1, I1A and I2 wherein
 R⁵⁻¹⁰ are selected from alkyl, alkoxy, thioalkyl or fluoroalkyl groups.

The introduction of such lateral side chains R⁵⁻¹⁰ into the anthracene
 group improves their solubility and therefore their solution

processibility. Furthermore, the presence of such side chains also renders these materials effective as *n*-type semiconductors. The electron-withdrawing nature of fluoroalkyl substituents will also lower the HOMO further and result in a more stable material, which is less susceptible to oxidation.

The polymers according to the invention show advantageous solubility properties which allow production processes using solutions of these compounds. Thus films, including layers and coatings, may be generated by low cost production techniques, e.g., spin coating. Suitable solvents or solvent mixtures comprise alkanes and/ or aromatics, especially their fluorinated derivatives.

Semiconductor devices like OFETs, where an organic semiconductive material is arranged as a film between a gate-dielectric and a drain and a source electrode, are generally known in prior art and described for example in US 5,892,244, WO 00/79617, US 5,998,804. Due to the advantages, like low cost production using the solubility properties of the compounds according to the invention and thus the processibility of large surfaces, preferred applications of these FETs are such as integrated circuitry, TFT-displays and security applications.

In security applications, OFETs and other devices with semiconductive materials, like transistors or diodes, may be used for ID tags or security markings to authenticate and prevent counterfeiting of documents of value like banknotes, credit cards or ID cards, national ID documents, licenses or any product with money value, like stamps, tickets, shares, cheques etc..

The materials according to the invention may also be used as a means to produce macroscopically aligned electroluminescent layers, for example in organic light emitting devices or diodes (OLEDs). Such OLEDs can be used as emitters of linear or circular polarized light, suitable in display applications or as backlight of liquid

crystal displays, security elements, antiglare lighting elements, horticultural lighting elements etc..

5 Common OLEDs are typically realized using multilayer structures. An emission layer is generally sandwiched between one or more electron-transport and/ or hole-transport layers. By applying a voltage, electrons and holes as charge carriers move towards the emission layer where their recombination leads to the excitation and hence luminescence of the lumophor units contained in the emission
10 layer. The inventive compounds, materials and films may be employed in one or more of the charge transport layers and/ or in the emission layer, corresponding to their electrical and/ or optical properties. Furthermore their use within the emission layer is especially advantageous, if the compounds, materials and films
15 according to the invention show electroluminescent properties themselves or comprise electroluminescent groups or compounds. The selection, characterization as well as the processing of suitable monomeric, oligomeric and polymeric compounds or materials for the use in OLEDs is generally known by a person skilled in the art, see,
20 e.g., Meerholz, Synthetic Materials, 111-112, 2000, 31-34, Alcala, J. Appl. Phys., 88, 2000, 7124-7128 and the literature cited therein.

According to another use, the inventive compounds, materials or films, especially those which show photoluminescent properties, may
25 be employed as materials of light sources, e.g., of display devices such as described in EP 0 889 350 A1 or by C. Weder et al., Science, 279, 1998, 835-837.

According to another use, the inventive compounds, materials or
30 films can be used alone or together with other materials in or as alignment layers in LCD or OLED devices, as described for example in US 2003/0021913. The use of charge transport compounds according to the present invention can increase the electrical conductivity of the alignment layer. When used in an LCD, this
35 increased electrical conductivity can reduce adverse residual dc effects in the switchable LCD cell and suppress image sticking or, for

example in ferroelectric LCDs, reduce the residual charge produced by the switching of the spontaneous polarisation charge of the ferroelectric LCs. When used in an OLED device comprising a light emitting material provided onto the alignment layer, this increased electrical conductivity can enhance the electroluminescence of the light emitting material. The compounds or materials according to the present invention having mesogenic or liquid crystalline properties can form oriented anisotropic films as described above, which are especially useful as alignment layers to induce or enhance alignment in a liquid crystal medium provided onto said anisotropic film. The materials according to the present invention may also be combined with photoisomerisable compounds and/or chromophores for use in or as photoalignment layers, as described in US 2003/0021913.

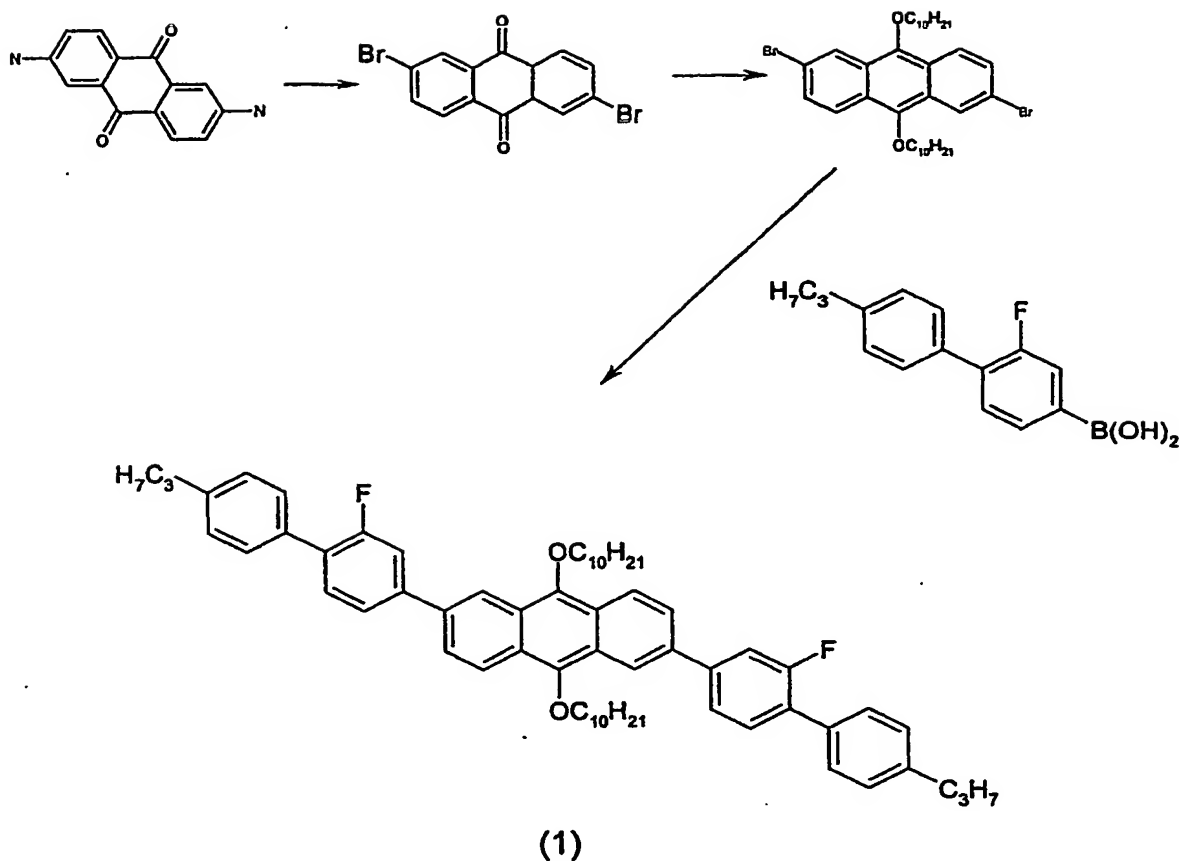
The examples below serve to illustrate the invention without limiting it. In the foregoing and the following, all temperatures are given in degrees Celsius, and all percentages are by weight, unless stated otherwise. The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds: K = crystalline; N = nematic; S = smectic; N*, Ch = chiral nematic or cholesteric; I = isotropic. The numbers between these symbols indicate the phase transition temperatures in degree Celsius.

Example 1

Synthesis of 2,6-di-4'-(2'-Fluoro 4-*n*-propylbiphenyl)-9,10-didecoxyanthracene. (Compound 1)

Compound (1) was prepared as shown below.

- 46 -

Step 1

CuBr₂ (200g, 0.857 moles), 90% ^tBuNO₂ (186 ml, 1.40 moles) and MeCN (3000ml) were added together and heated to 60 °C with rapid stirring. 2,6-diaminoanthraquinone (100g, 0.420 moles) was added dropwise as a semi-solid solution in MeCN (1000ml). N₂ and Br₂ were evolved and the reaction mixture turned black (CuO) with a 6°C exotherm. A brown solid was filtered off and then partially redissolved at reflux in cyclohexanone (4lt) and the hot solution was gravity filtered through at 100°C using a ceramic filter. The preparation was repeated at the same scale six times to yield 205g of crude product. The combined batches were recrystallised with hot filtration using cyclohexanone to yield 180g of pure product. GC/MS analysis showed a pure product with a mass ion (M⁺ 366) together with trace

amounts of a tribrominated and monobrominated impurities. Proton NMR spectroscopy confirmed the structure.

Step 2

5

2,6-dibromoanthraquinone (30g, 0.0819 moles), sodium dithionite (31g, 0.18moles), sodium hydroxide 12g, 0.3 moles), Tetrabutylammoniumiodide(7.2g, 0.00324 moles), demineralised water (30ml) & cyclohexanone (500ml), were heated under reflux at 97°C for 5 hours under a nitrogen atmosphere. The reaction mixture turned from purple to dark brown, and a precipitate of the anthraquinone disodium salt appeared.

10

15

A solution of 1-bromo-decane (37.5ml, 0.180 moles) was added at 60°C to the reaction mixture, together with an additional 50mls of demineralised water, to redissolve the disodium salt. The reaction mixture was then heated at reflux for a further 24 hours. The crude product was isolated by conventional extraction and aqueous workup to yield 26g of material. The crude material was purified by recrystallisation from ethyl acetate, to yield pure 2,6-dibromo-9,10-didecoxyanthracene as a pale yellow solid.

20

Step 3

25

2,6-dibromo-9,10-didecoxyanthracene (4g, 6.167mmoles), 2'-Fluoro 4-*n*-propylbiphenyl-4'-boronic acid (3.3g, 12.786mmoles), sodium carbonate (1.5g, 14.151mmoles), 1,1 Bis diphenylphosphino ferrocene di chloro palladium (II) (0.2g, 0.245mmoles) and 1,4-dioxane (20ml) were combined under a nitrogen atmosphere and heated at 70°C for 18 hours. The reaction mixture went a dark blue colour and was added to methanol. The precipitate was filtered filtered off and the organic portion was extracted using warm THF, and the THF solution was filtered through a glass fibre filter mat. The crude product was precipitated with methanol & washed with 40-60 petrol.

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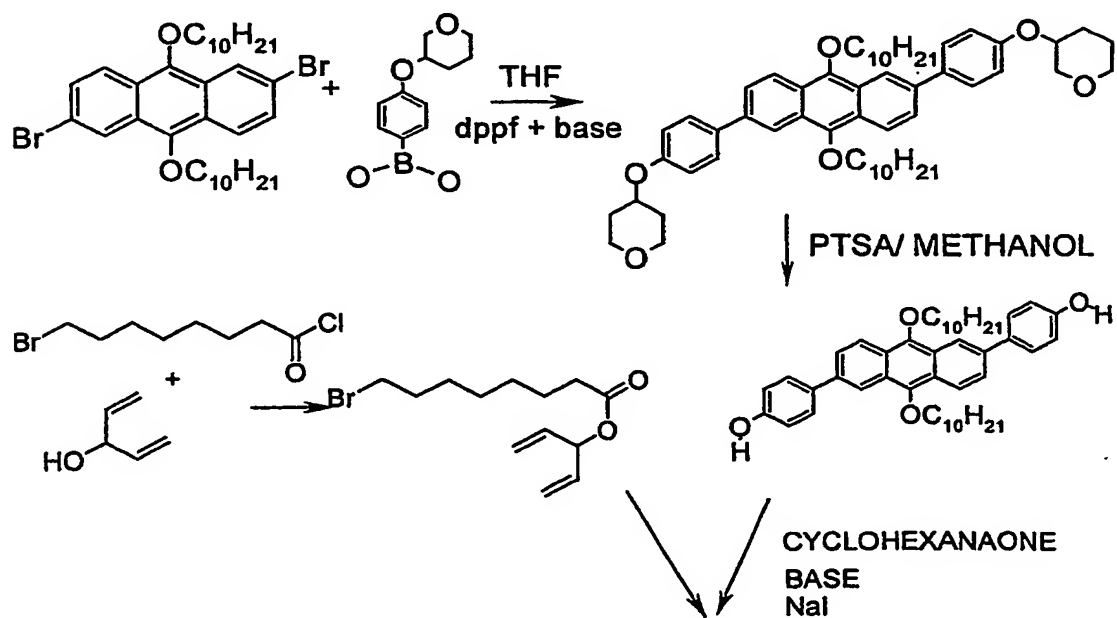
The crude product was purified by column chromatography, eluting over silica with a 95:5 petrol:ethyl acetate mixture, increasing the eluent strength with THF. The chromatographed product was recrystallised from an IPA – THF mixture to yield 2,6-di-4'-(2'-Fluoro 4-*n*-propylbiphenyl)-9,10-didecoxyanthracene, a bright yellow pure material. 2.2g yield. Proton NMR spectroscopy and GC-MS confirmed the structure.

The pure compound exhibits the following mesophase behaviour
K 148 N 215 I heating
I 213 N 137 K cooling

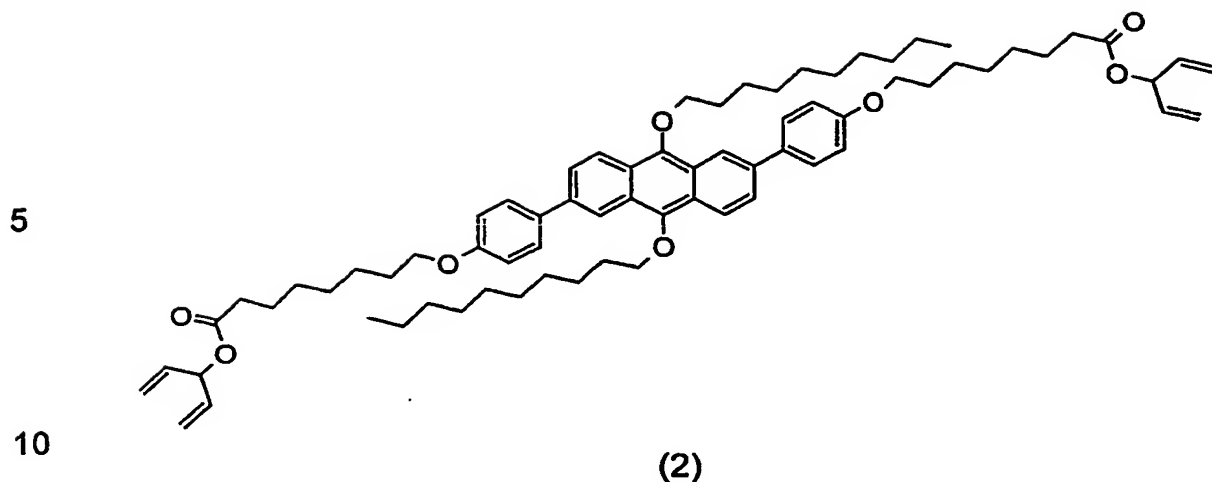
Example 2

Synthesis of 2,6-bis(1-(4-[7-(1-vinyl-allyloxy-carbonyl)heptyloxy]phenyl)-9,10-didecoxyanthracene

Compound (2) was prepared as shown below.



35



Step 1

15 2,6-dibromo-9,10-didecoxyanthracene (6g, 9.125mmoles), 4-dihydropyranyloxyboronic acid (4.4g, 20mmoles), sodium carbonate (5.2g, 49.7mmoles), 1,1 Bis diphenylphosphino ferrocene di chloro palladium (II) (0.56g, 0.696mmoles) THF (150ml) & demineralised water (10ml) were combined under a nitrogen atmosphere and heated at reflux for 18 hours.

20

Crude 2,6-di-4-(4-dihydropyranyloxyphenyl)-9,10-didecoxyanthracene precipitated from the reaction mixture and was filtered off. The crude product was used without further purification. Yield 5g.

25

Step 2

2,6-di-4-(4-dihydropyranyloxyphenyl)-9,10-didecoxyanthracene (5g, 5.930mmol), was dissolved in a methanol / THF mixture (1:5 500ml). p-toluenesulphonic acid (4g) was added and the reaction mixture was heated with stirring to 30°C o/n. The resultant solution was evaporated to low volume and the crude product was precipitated with ethanol/water, filtered off and washed with ethanol to yield pure 2,6-di-4-(4-hydroxyphenyl)-9,10-didecoxyanthracene 4g, Proton NMR spectroscopy and GC-MS confirmed the structure.

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35

Step 3

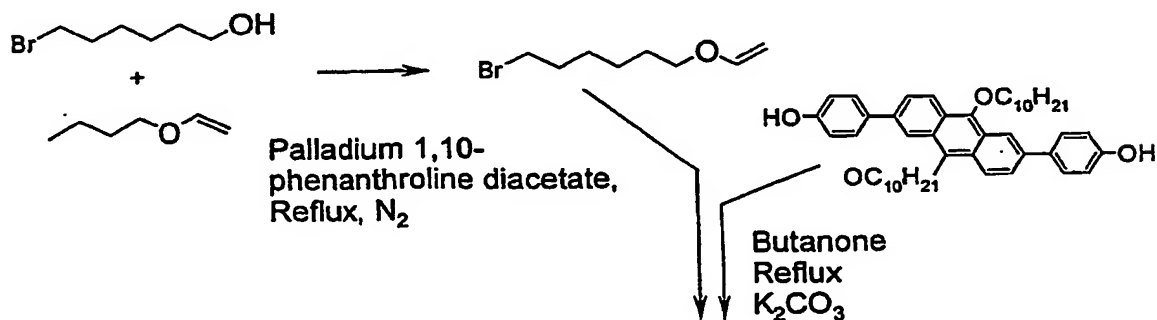
2,6-di-4-(4-hydroxyphenyl)-9,10-didecoxyanthracene (3.0g, 4.44 mmol), potassium iodide (1.499g, 10mmol), potassium carbonate (2.7g, 20mmol), Tetrabutylammoniumiodide (0.2g) & butanone (100ml), were heated to reflux @ 80°C. A solution of 7-bromoheptanoic acid, 2-hydroxy-1,3-pentadienyl ester (2.89g, 10mmol) was added to the reaction mixture, and refluxed overnight. The crude product was isolated by conventional extraction and aqueous workup. The crude product was purified by column chromatography, eluting over silica with a 90:10 petrol:ethyl acetate mixture. The chromatographed product was recrystallised from an IPA – THF mixture to yield, 2,6-bis(1-(4-[7-(1-vinyl-allyloxy-carbonyl)heptyloxy]phenyl)-9,10-didecoxyanthracene as an off white-yellow material. 2.2g yield (20%). Proton NMR spectroscopy and GC-MS confirmed the structure.

The pure material exhibited a melting point of 133°C.

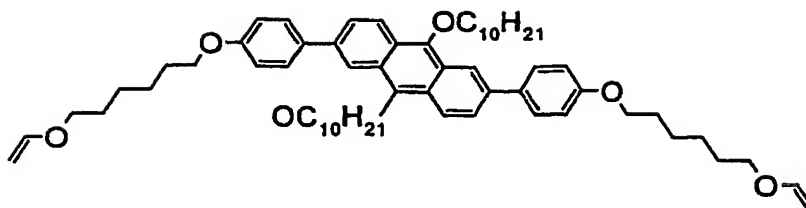
Example 3

Synthesis of 2,6-bis(1-(4-[7-(1-vinyloxy)hexyloxy]phenyl)-9,10-didecoxyanthracene.

Compound (3) was prepared as shown below.



- 51 -



5

(3)

Step 1

10 6-bromo-1-vinyloxyhexane was prepared according to the method of Percec et al as described in Polymer Bulletin 1991, 26, 15-22.

Step 2

15 Compound (3) was prepared in an analogous procedure to that of compound (2)

2,6-di-4-(4-hydroxyphenyl)-9,10-didecoxyanthracene (3.0g, 4.44 mmol), potassium iodide (1.499g, 10mmol), potassium carbonate 20 2.7g, 20mmol), Tetrabutylammoniumiodide (0.2g) & butanone (100ml), were heated to reflux @ 80°C. A solution of 6-bromo-1-vinyloxyhexane (5g, 24mmol) was added to the reaction mixture, and refluxed overnight. The crude product was isolated by conventional extraction and aqueous workup. The crude product was purified by column chromatography, eluting over silica with a 90:10 petrol:ethyl acetate mixture. The chromatographed product was recrystallised 25 from an IPA = THF mixture to yield, 2,6-bis(1-(4-[7-(1-vinyloxy)hexyloxy]phenyl)-9,10-didecoxyanthracene as an off white-yellow material. 0.6g yield (6%). Proton NMR spectroscopy and GC-MS confirmed the structure. 30

The pure material exhibited a melting point of 131°C.

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Patent Claims

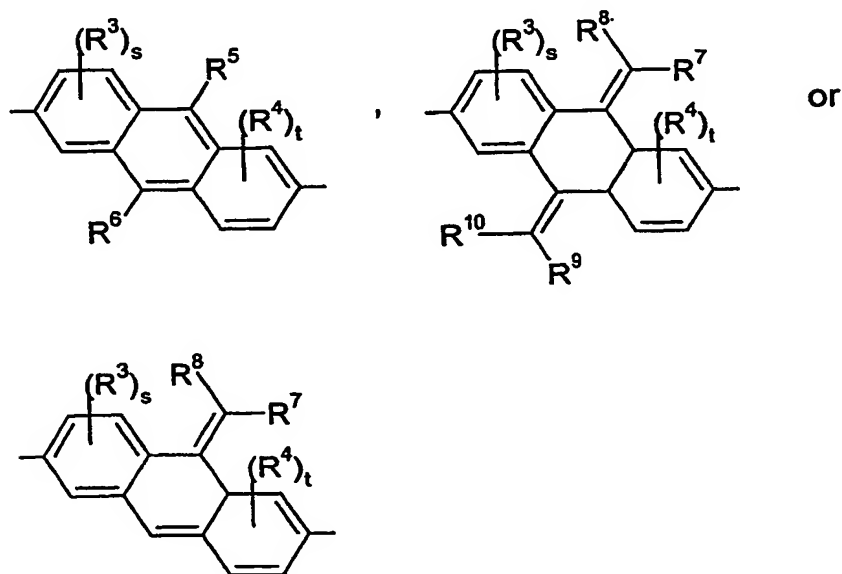
1. Compounds, including reactive and non-reactive monomers, oligomers and polymers, comprising one or more identical or different groups of formula I

-(G)_g-

I

wherein

G is, in case of multiple occurrence independently of one another,



R³ to R¹⁰ are independently of each other F, Cl, Br, I, CN, NO₂, NCS, SF₅ or straight chain or branched alkyl having 1 to 30 C-atoms that is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, and in which one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CY¹=CY²-

or $\text{-C}\equiv\text{C-}$ in such a manner that O and/or S atoms are not linked directly to one another, or P-Sp,

5 R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms,

P is a polymerisable or reactive group,

10 Sp is a spacer group or a single bond,

s and t are independently of each other 0, 1, 2 or 3,

15 g is, in case of multiple occurrence independently of one another, 1, 2 or 3.

2. Compounds according to claim 1, comprising at least one recurring unit of formula I1

20 $\text{--[}(\text{G})_g\text{-(A)}_a\text{]}_z\text{--}$ I1

wherein G and g have the meanings of formula I,

25 A is, in case of multiple occurrence independently of one another, $\text{-CX}^1\text{=CX}^2\text{-}$, $\text{-C}\equiv\text{C-}$, an aromatic or alicyclic ring or a group comprising two or more fused aromatic or alicyclic rings, wherein these rings optionally contain one or more hetero atoms selected from N, O and S, and are optionally mono-

30 or polysubstituted by R^3 as defined in formula I, X^1 and X^2 are independently of each other H, F, Cl or CN,

a is, in case of multiple occurrence independently of one another, 0 or 1,

35 z is an integer ≥ 1 ,

wherein in case of multiple occurrence the groups $[(G)_g-(A)_a]$ can be identical or different.

- 5 3. Compounds according to claim 1 or 2, selected of formula I1A



wherein G, g, A, a and z have the meanings of formula I1,

10

R^1 and R^2 have independently of each other one of the meanings of R^3 in formula I, or denote $B(OR')(OR'')$ or $SnR^0R^{00}R^{000}$,

15

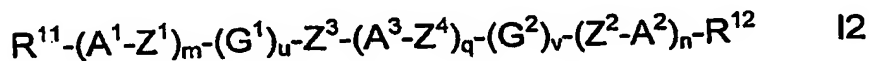
R^{0-000} are independently of each other H or alkyl with 1 to 12 C-atoms,

20

R' and R'' are independently of each other H or alkyl with 1 to 12 C-atoms, or OR' and OR'' together with the boron atom may also form a cyclic group having 2 to 10 C atoms.

4. Compounds according to claim 1 or 2, selected of formula I2

25



wherein

30

G^1 and G^2 have independently of each other one of the meanings of G in formula I,

R^{11} and R^{12} have independently of each other one of the meanings of R^3 in formula I,

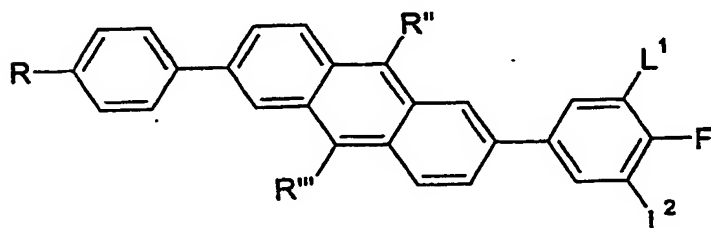
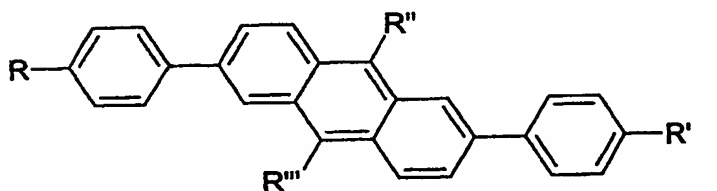
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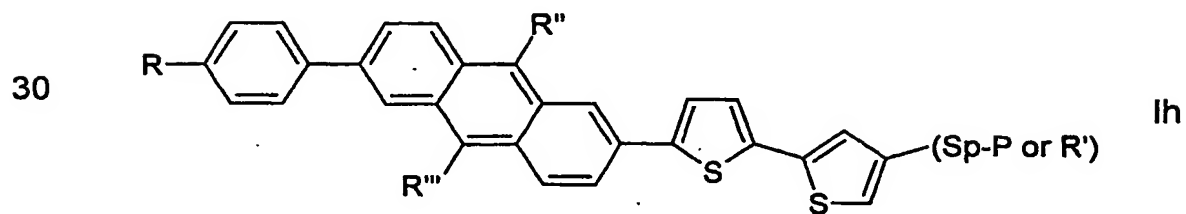
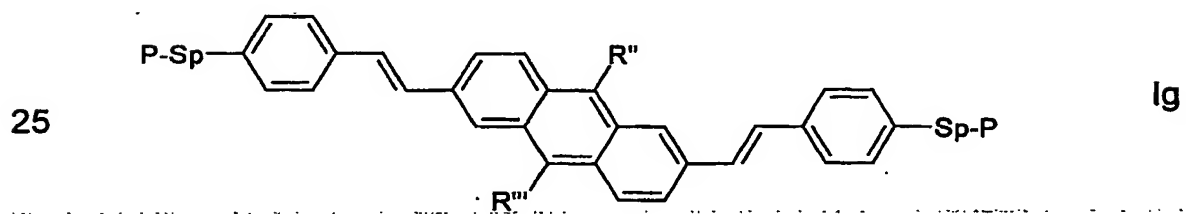
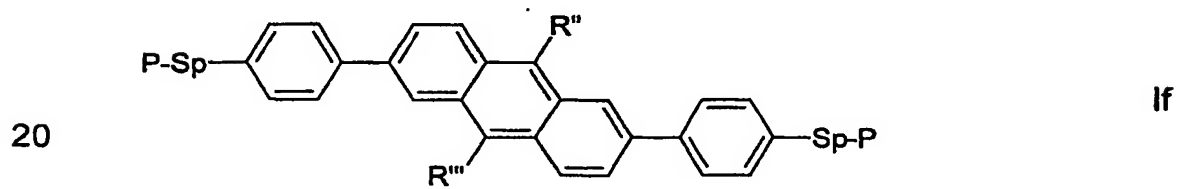
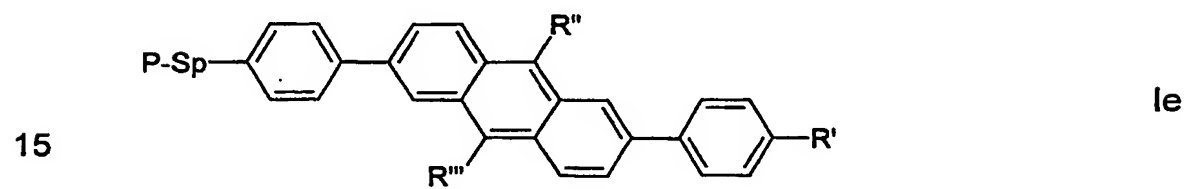
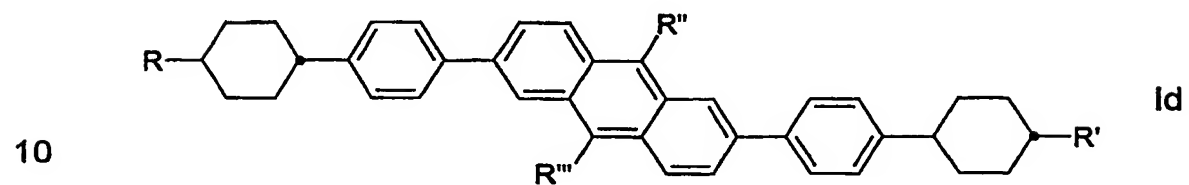
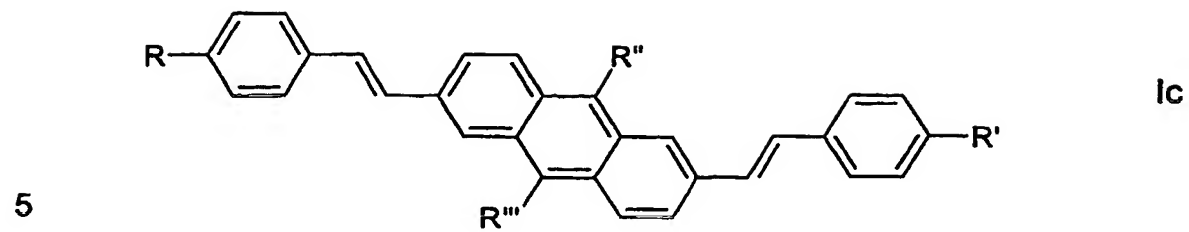
A^1 to A^3 have independently of each other one of the meanings of A in formula I1,

- 5 Z^1 to Z^4 are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -S-CO-, -CO-S-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CR⁰-, -CY¹=CY²-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,
- 10 Y^1 and Y^2 are independently of each other H, F, Cl or CN,
- R^0 and R^{00} have the meanings given in formula I,
- 15 m, n and q are independently of each other 0, 1, 2 or 3,
- u and v are independently of each other 0, 1 or 2, with $u+v > 0$.
- 20 5. Compounds according to claim 3 or 4, characterized in that z is an integer from 2 to 5000.
6. Compounds according to claim 3 or 4, characterized in that z is an integer from 1 to 15.
- 25 7. Compounds according to at least one of claims 3 to 6, characterized in that one or both of R^1 and R^2 denote P-Sp-.
- 30 8. Compounds according to at least one of claims 1 to 7, characterized in that R^3 and R^4 are selected from F, Cl, CN, alkyl, oxaalkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl with 1 to 15 C-atoms or alkenyl, alkenyloxy or alkynyl with 2 to 15 C-atoms.
- 35 9. Compounds according to at least one of claims 1 to 8, characterized in that R^{5-10} are selected from F, Cl, CN, C₁-C₂₀-alkyl that is optionally substituted with one or more fluorine

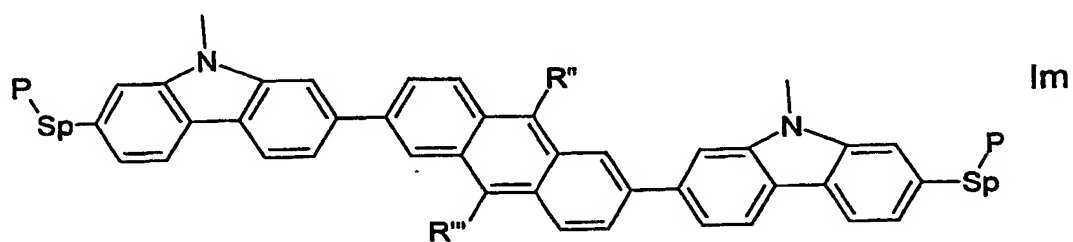
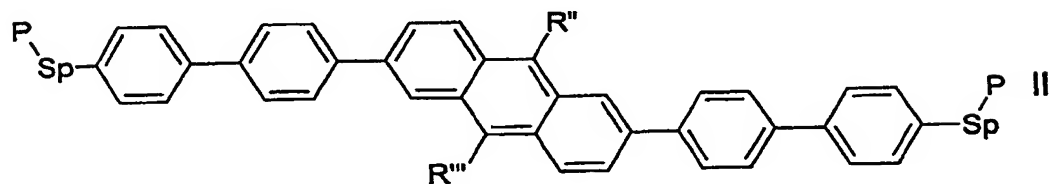
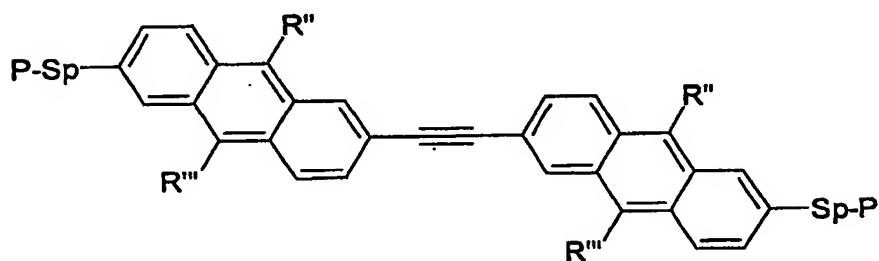
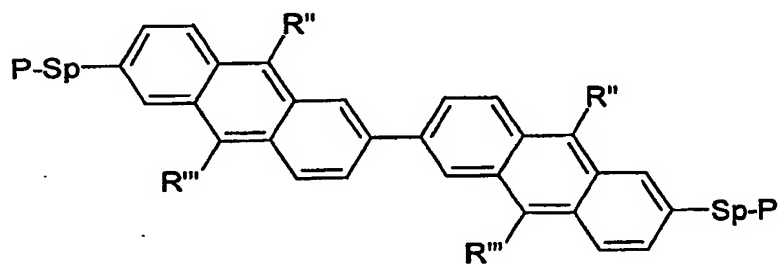
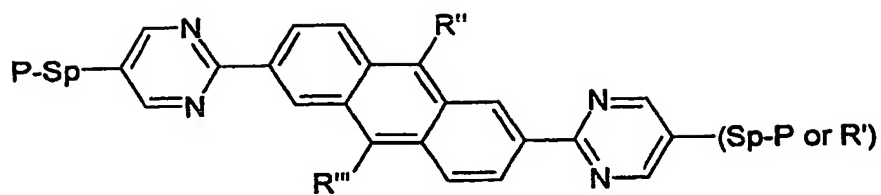
atoms, C₁-C₂₀-alkenyl, C₁-C₂₀-alkynyl, C₁-C₂₀-alkoxy, C₁-C₂₀-thioalkyl, C₁-C₂₀-silyl, C₁-C₂₀-ester, C₁-C₂₀-amino, C₁-C₂₀-fluoroalkyl, (CH₂CH₂O)_m with m being an integer from 1 to 6.

- 5 10. Compounds according to at least one of claims 2 to 9,
characterized in that A and A¹⁻³ are selected from furane-2,5-
diyl, thiophene-2,5-diyl, thienothiophene-2,5-diyl,
dithienothiophene-2,6-diyl, pyrrol-2,5-diyl, 1,4-phenylene,
10 azulene-2,6-diyl, pyridine-2,5-diyl, pyrimidine-2,5-diyl,
naphthalene-2,6-diyl, 1,2,3,4-tetrahydro-naphthalene-2,6-diyl,
indane-2,5-diyl, or 1,4-cyclohexylene wherein one or two non-
adjacent CH₂ groups are optionally replaced by O and/or S,
wherein these groups are unsubstituted, mono- or
15 polysubstituted by R³ as defined in claim 1.
11. Compounds according to at least one of claims 1 to 10,
characterized in that P is a vinyl ether, propenyl ether or
oxetane group.
- 20 12. Compounds according to at least one of claims 1 to 11, selected
from the following formulae





35



wherein

35 R and R' have independently of each other one of the meanings of R¹ in formula I1 and are preferably

straight chain alkyl or alkoxy with 1 to 12 C-atoms or alkenyl, alkenyloxy or alkynyl with 2 to 12 C-atoms,

- 5 R" and R''' have independently of each other one of the meanings of R⁵ in formula I and are preferably straight chain alkyl, alkoxy, thioalkyl or fluorinated alkyl with 1 to 20 C-atoms, very preferably with 5 to 15 C-atoms,
- 10 P and Sp have the meanings given in formula I, and
- L¹ and L² are independently of each other H or F, and
- 15 the aromatic rings in the above formulae are optionally substituted with 1, 2 or 3 groups R³ as defined in formula I.
13. Compounds according to at least one of claims 1 to 11, characterized in that it comprises at least one repeating unit selected from formulae Ia to Im of claim 12, without the groups
- 20 R and P-Sp.
14. LC medium comprising at least one compound according to at least one of claims 1 to 13.
- 25 15. Polymerisable LC material comprising at least one compound according to at least one of claims 1 to 12 and optionally at least one further compound, wherein at least one of said compounds is polymerisable.
- 30 16. Polymer obtained by polymerising a compound according to at least one of claims 1 to 13 or a polymerisable LC material according to claim 15.
- 35 17. Anisotropic polymer obtained by polymerising a compound according to at least one of claims 1 to 13 or a polymerisable LC

material according to claim 15 in its oriented state in form of a film.

- 5 18. Semiconductor or charge transport material comprising at least one compound, polymerisable LC material or polymer according to at least one of claims 1 to 17.
- 10 19. Light-emissive material comprising at least one compound, polymerisable LC material or polymer according to at least one of claims 1 to 17.
- 15 20. Use of a compound, polymerisable LC material, polymer, semiconductor or light-emitting material according to at least one of claims 1 to 19 in electrooptical displays, LCDs, eLCDs, optical films, polarisers, compensators, beam splitters, reflective films, alignment layers, colour filters, holographic elements, hot stamping foils, coloured images, decorative or security markings e.g. for consumer objects or documents of value, LC pigments, adhesives, synthetic resins with anisotropic mechanical
- 20 properties, cosmetics, pharmaceuticals, diagnostics, nonlinear optics, optical information storage, as chiral dopants, in electronic devices like for example OFETs as components of integrated circuits (IC), as thin film transistors (TFT) in flat panel display applications or for Radio Frequency Identification (RFID)
- 25 tags, in semiconducting or light-emitting components of organic light emitting diode (OLED) applications, electroluminescent displays or backlights of LCDs, for photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors, or for electrophotographic applications or electrophotographic
- 30 recording or as alignment layer in LCD or OLED devices.
- 35 21. Optical, electrooptical or electronic device, LCD, eLCD, OLED, OFET, IC, TFT or alignment layer characterized in that it comprises a compound, polymerisable LC material, polymer, semiconductor or light-emitting material according to at least one of claims 1 to 19.

5 22. TFT or TFT array for flat panel displays, RFID tag, electroluminescent display or backlight comprising a compound, polymerisable LC material, polymer, semiconductor or light-emitting material or device according to at least one of claims 1 to 19 or 21.

10 23. Security marking or device comprising a compound, polymerisable LC material, polymer, semiconductor or light-emitting material or device according to at least one of claims 1 to 19, 21 or 22.

15

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30

35

Abstract

The invention relates to novel 9- and/or 10-substituted anthracenes,
to their use in liquid crystal, light-emitting or semiconducting
5 materials and devices, in anisotropic polymers, optical, electrooptical,
decorative, security, cosmetic, diagnostic, electric, electronic, charge
transport, semiconductor, optical recording, electroluminescent,
photoconductor or electrophotographic applications, and to liquid
10 crystal, light-emitting and semiconducting materials, polymers and
devices comprising them.

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